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- Concept Map

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CHEMICAL BONDING
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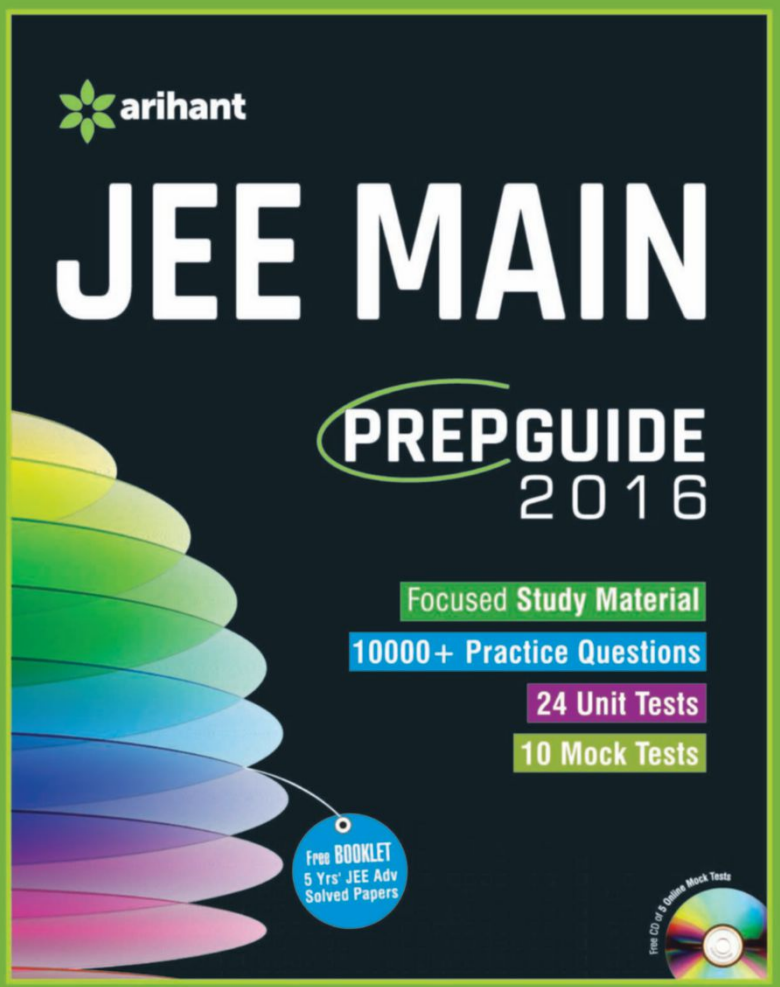

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CHEMISTRY Spectrum

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120 DAYS COUNTDOWN
towards JEE 2016

DAY 1
- Some Basic Concepts of Chemistry
- Matter, Classification of Matter, Units & Measurement, Significant Figure, Errors

DAY 2
- Laws of Chemical Combination and Stoichiometry

DAY 3
- Stoichiometry (Continued)

DAY 4
- Stoichiometry (Practice)

DAY 5
- Practice problems related to some basic concepts of chemistry

DAY 6
- Structure of Atom
- Preliminary Theories, Developments Leading to Bohr's Model, (PE Effect, EM Waves Spectrum, Black Body Radiation)

DAY 7
- Bohr's Model, Hydrogen Spectrum and Numerical Related to it. Bohr's Sommerfeld Model

DAY 8
- Bohr's Model, Hydrogen Spectrum and Numerical Related to it. Bohr's Sommerfeld Model

DAY 9
- Developments Leading to Quantum Mechanical Model (de-Broglie + Heisenberg's Principles)
- Quantum Mechanical Model

DAY 10
- Electronic Configuration of atoms (Aufbau Principles and Hund's Rule)
- Quantum Numbers

DAY 11
- Practice Problems, Related to Atomic Structure

DAY 12
- Periodic Classification
- Basics

DAY 13
- Periodic Properties

DAY 14
- Practice Problems Related to Periodic Classification and Periodic Properties

DAY 15
- Chemical Bonding
- Basics (Kossel Lewis Approach, Ionic Bonding, Covalent Bonding, Coordinate Covalent Bonding)

DAY 16
- Covalent Bond (Advanced Approach), Hybridisation and VSEPR Theory

DAY 17
- Covalent Bonding, Bond Parameter, Dipole Moment, Resonance, MOT

DAY 18
- Practice Problems Related to Chemical Bonding

MENTORS VOICE Topics till 18th day are taken under general chemistry. These all the topics are very important to built the foundation of chemistry. Topics of day 1 and 2 are relevant from board's perspective. Stoichiometry, Photoelectric effect, Bohr's model, Hydrogen spectrum, quantum numbers, periodic properties, Hybridisation, VSEPR theory, dipole moment, resonance and MOT are the concepts of importance as most of the direct questions in JEE are asked from these concepts frequently. Remember all of these topics belong to class 11th syllabus and the approximate coverage of this portion in JEE reaches to approximately 15%. As most of the chapters of general chemistry involve numericals that's why it is also important to have a good practice of numericals. For this sake it is advisable to devote a separate one day for problem practice as shown in planner. Random testing is required initially to test your understanding of first 18 days. For stoichiometric calculations develop your own shortcuts and it is also suggestive to use approximation technique in calculations to save time. Atomic structure has overlapping with the Modern physics portion of physics so in deep study of this portion will prove very helpful in gripping the Modern physics portion. As most of the part of first 18 days serves as the basis for gripping the subject, thus it is advisable not to move on day 19th topics until you develop confidence in these topics.

DAY 19
- States of Matter (Gaseous State Proper)
- Gaseous State, Measurable Properties of Gases, Gaseous Laws

DAY 20
- KTG, Ideal and Real Gases.

DAY 21
- States of Matter (Liquid state), van der Waals' equation & Critical Phenomenon, Matter Properties, Vapour pressure, Viscosity, Surface Tension

DAY 22
- Problem Practice Related to States of Matter

DAY 23
- Thermodynamics
- Basics

DAY 24
- Problem Practice Related to Thermodynamics

DAY 25
- Thermochemistry

DAY 26
- Thermochemistry

DAY 27
- Problems practice related to thermochemistry

DAY 28
- Chemical Equilibrium
- Upto Le Chatelier Principles

DAY 29
- Ionic Equilibrium
- Ostwald's Dilution law, Concept of Electrolyte, Acid and Bases

DAY 30
- Ionic and Solubility Product, Common Ion Effect

DAY 31
- pH, Buffers, Salt Hydrolysis, Indicators

DAY 32
- Problems Practice Related to Chemical Equilibria

DAY 33
- Problems practice related to ionic equilibria

DAY 34
- Redox
- Reduction, Oxidation, Oxidation Number, Balancing of Equations

DAY 35
- Electrochemistry
- Electrolysis, Electrochemical Cells and Electrolytic Cells

DAY 36
- Concept of Conductivity by Electrolytes upto Kohlrausch Law

DAY 37
- Nernst Equation, Gibb's free Energy Relation, Batteries and Corrosion

DAY 38
- Problems Related to Redox and Electrochemistry

MENTORS VOICE All topics of this segment belong to physical chemistry. This branch of chemistry has many similarities with physics in nature, so, take physics like approach to capture this portion of chemistry. The topics of interest are gas laws and gas equation especially van der Waal's modification, concept of entropy, Gibb's free energy, various enthalpy related problems in connection with chemical equations, Le Chatelier principle, solubility product, common ion effect, pH, buffers, salt hydrolysis and its applications, electrochemical series and its applications, electrochemical cells, Nernst equation and batteries (especially corrosion). Direct questions can be easily framed on these topics. Some questions of mixed nature are also seen. It is advisable to take electrochemistry with redox as latter is helpful in understanding the former. Try to develop direct formulas for solubility product, pH and salt hydrolysis to save time. Random and planned testing is required to judge the exact learning. For topics mentioned above learning with direct solved examples will be beneficial.

DAY 39
- Hydrogen

DAY 40
- *s*-block Elements
- Alkali Metals

DAY 41
- Alkaline Earth Metals

DAY 42
- Problems practice related to hydrogen and *s*-block elements

DAY 43
- *p*-block elements
- Group 13 Elements

DAY 44
- Group 14 Elements

DAY 45
- Problems practice related to group13 and 14 respectively

DAY 46
- Group 15 Elements

DAY 47
- Group 15 Elements

DAY 48
- Group 16 Elements

DAY 49
- Group 16 Elements

DAY 50
- Problems practice related to group 15 and 16 respectively

DAY 51
- Group 17 Elements

DAY 52
- Group 17 Elements + Group 18 Elements

DAY 53
- Problems practice related to group 17 and 18 respectively

DAY 54
- Extraction and Isolation of Metals

DAY 55
- Metallurgy

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DAY 56
- Problems practice related to metallurgy

MENTORS VOICE All topics of this segment belong to inorganic chemistry. This branch of chemistry is very vast and requires picturisation technique to capture. Repeated readings (without memorisation) are required to the topics. The topics of special interest are H_2O_2, *s*-block elements (especially Li, Na, K, Be, Mg and Ca) and their compounds, among *p*-block B, C, N, O, F, P, S, Cl and Xe with especial reference to oxy acids of N, P, S, Inter halogen compounds, compounds of Xe. The emphasis must be laid on the structures in case of oxy acids and compounds of Xe. The study about compounds like NH_3, HNO_3, H_2SO_4, H_3PO_4 from properties point of view is very important. In case of HNO_3 emphasise more on type of nitrogen oxide or related product formed during the reaction rather than the oxidation product. Elements of 2nd period are called naughty elements as all of these show different properties than the fellow members of their group due to their small size. Most of the questions framed and asked on these elements only. Questions on B are very frequent. Use random testing for Topics till Day 56th for self-analysis and use planned tests in two sections, i.e.

(a) Day 1st to 38th

(b) Day 39th to 56th

for proper assessment and to gain confidence.

DAY 57
- Solid State
- Upto Packing in Solids

DAY 58
- Imperfection in Solid and Properties of Solids

DAY 59
- Practice Problems Related to Solid State

DAY 60
- Solution Basics, upto Roult's Law

DAY 61
- Colligative Properties

DAY 62
- Abnormal colligative properties

DAY 63
- Practice Problem Related to Solutions

DAY 64
- Chemical Kinetics, Rate of a chemical reaction and factors influencing rate of a reaction

DAY 65
- Order and molecularity of a reaction, Integrated rate equation

DAY 66
- Pseudo first order reaction, Temperature dependence on the rate of a reaction and collision theory.

DAY 67
- Problems Related to Chemical Kinetics

DAY 68
- Surface Chemistry
- Adsorption and Catalysis

DAY 69
- Colloidal State

DAY 70
- Problem Practice related to Surface Chemistry

DAY 71
- *d* & *f* Block elements
- Transition Elements

DAY 72
- Inner Transition Elements

DAY 73
- Coordination Compounds
- Nomenclature & Isomerism

DAY 74
- VBT and CFT, Bonding in organo metallic Compounds, Stability of Coordination Compounds

DAY 75
- Problems Related to Coordination chemistry

MENTORS VOICE This segment contains both physical and inorganic portions. The topics of special interest are solid state, colligative properties, chemical kinetics with special emphasis on order and molecularity of reactions, pseudo unimolecular reactions, radioactivity in relation to chemical kinetics, catalysis in general, colloidal state, lanthanide contraction, variable oxidation states in transition elements,nomenclature and isomerism in coordination compounds, VBT and CFT in coordination compounds.

This segment contains three very important chapters, i.e. solid state, surface chemistry and coordination compounds begin this complete section everyday with randomized check through random test to analyses your points of emphasis for your preparation.

DAY 76
- IUPAC Nomenclature

DAY 77
- Problems practice related to nomenclature

DAY 78
- Structure Isomerism, Purification of Organic Compounds

DAY 79
- Problems related to structural isomerism and purification of organic compounds

DAY 80
- Stereo Isomerism

DAY 81
- Stereo Isomerism

DAY 82
- Problems practice related to stereoisomerisms

DAY 83
- Electron Displacement in a Molecule
- Permanent Effect, Inductive Effect, Conjugation

DAY 84
- Problems practice related to Permanent effect, Inductive effect and conjugation

DAY 85
- Mesomeric Effect, Resonance

DAY 86
- Hyper conjugation, Electromeric Effect, Inductomeric Effect

DAY 87
- Problems practice related to topics in days 85 and 86

DAY 88
- Types of Organic Reaction, Substitution Reaction

DAY 89
- Problems practice related to substitution reaction

DAY 90
- Addition Reaction

DAY 91
- Elimination Reaction

DAY 92
- Addition-Elimination Reaction

DAY 93
- Problems practice related to topics of days 90, 91 and 92

DAY 94
- Rearrangement Reaction

DAY 95
- Hydrocarbon
- Alkanes

DAY 96
- Problems practice related to alkanes

DAY 97
- Alkenes

DAY 98
- Problems practice related to alkenes

DAY 99
- Alkynes

DAY 100
- Problems practice related to alkynes

DAY 101
- Benzene

DAY 102
- Halogen containing Aliphatic Compounds

DAY 103
- Problems practice related to days 101 and 102 topics

DAY 104
- Halogen Containing Aromatic Compounds & Related Problems

DAY 105
- Aliphatic Alcohol

DAY 106
- Problems practice related to aliphatic alcohol

DAY 107
- Phenol + Ether

DAY 108
- Problems practice related to phenol + ether

DAY 109
- Aldehyde + Ketone

DAY 110
- Aldehyde + Ketone

DAY 111
- Problems practice related to aldehyde, ketone

DAY 112
- Carboxylic Acids

DAY 113
- Problems practice related to carboxylic acids

DAY 114
- Nitrogen Containing Compounds

DAY 115
- Problems practice related to *N*-containing compounds

DAY 116
- Biomolecules

DAY 117
- Polymers

DAY 118
- Environmental Chemistry

DAY 119
- Chemistry in Everyday Life

DAY 120
- Problems practice related to topics of days 116, 117, 118 and 119

MENTORS VOICE This last segment of your preparation is important as considerable numbers of questions are asked in JEE from this segment. This portion contains organic chemistry, which is also called conceptual chemistry. Correct orientation is required to capture this particular portion. Initial chapters upto day 94 are the fundamental chapters of this segment. IUPAC nomenclature and electron displacement in a molecule gives idea of structures of organic compounds, while Isomerism indicates the relationship between the structure and the reactions of organic compounds. The exposure to type of organic reactions is required to develop the complete logic. The chapters of utmost importance are Hydrocarbons and aldehydes and ketones. The chapters of moderate importance are halogen compounds, alcohols, nitrogen compounds and phenols. Questions on trends in the acidic and basic strength are frequently asked. Try to complete the schedule of last 20 days in 17 days (approx) as some loose days (days with lesser syllabus) are given in between. In the last 3 days use randomized testing of complete syllabus to filter your weaker portion and utilize these days to plug your weak points left.

For gaining the confidence afterwards use 2-3 simulator papers of full syllabus and try to complete them approximately 15 minutes before the stipulated time, so, that you can achieve the same under examination conditions of stress within the stipulated time.

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Revision The Ultimate Tool

"Toppers are in the habit of doing the things differently." Here surely the word **differently** has the *art of revision* or *reconciliation of learning* in its basis especially for the toppers of entrance examinations. Revision plays a prominent role in preparation of school, college or other entrance exams. Once syllabus is covered, revision is a mandatory requirement for better scoring, even, if one had not covered 100% of syllabus but only 70% or so, still he has to revise what syllabus has been covered.

How to Revise?

In a generalised methodology to be adopted during revision following steps are followed:

Step 1 Read your notes and seek answers to questions of your own. Try to be as active in your reading as possible. Your activeness can be in the form of talking to your self, walking around the room etc., Try to recollect what you have learned

Step 2 When you feel that you have understood and can remember what you have read. Then close your source of information (copy, book, notes etc.,)

Step 3 Try to recall the contents you were reading so far. You may pen down the same roughly and quickly on a new waste paper (if you are going for the first revision). This will help in filtering the remembered and non-remembered portions.

Step 4 Check the new notes with the old content. You may find certain points at which your memory is washed out. These points only require attention again. Try to answer a previous question paper i.e. past papers to see your progress once you revise.

Step 5 You may recheck your memory in random manner after a certain period of time too. The washed out memory points may increase or decrease. Repeated attention on these points can kill them then-n-there and boost up your confidence.

Step 6 Repetition of the same procedure for the same content many a times reduces the quantity of content requiring attention.

How to Revise Chemistry

We generally have a bad memory for chemical formulas, reactions, valency of elements, chemical structures, nature of the compounds etc in chemistry. Making mistakes because of the above reasons is always eminent, but a simple mistake changes the meaning of entire reaction. So

- During revision view the periodic table and familiarise with it frequently.
- Understand the basic difference between terminology like atomic weight, atomic number, element, compound, acid, base, salt, isotopes, isobars etc.
- Practice the reactions involving using combinations. Refer to the reactions having isotopes emission particles etc. in nuclear chemistry.
- Familiarise the stoichiometry principles of equalisation, clarify the differences of first order, second order, exothermic, endothermic and other types in writing the reactions.
- Be thorough in the valency of organic and inorganic elements, it helps you make no mistakes in representation of reactions. Even write them on your own during revision to see for possible mistakes.
- Solve the problems and exercises after revising the formulas and even practice derivations and structures of stereo-chemistry by precision during revision.

Special Mantras

Remember, revision is not something that starts in the end of academic session rather it is what you can do on daily basis; in fact you can initiate it right from the very first day of your learning.

Skills @ Effective Revision

While going for revisions keep following points in mind:

It is always better to prepare a revision schedule on daily basis and after making the schedule, it is must to possess the will to abide by that.

It is not necessary to revise large number of chapters every day. Revision must be slow and steady. It must be in the order to get firm grip on all types of questions asked on that topic.

Many times, we tend to miss out on writing some points when the teacher speaks. It is best to pen them down when they are still fresh in the memory.

Revise as many times as possible the entire subjects.

There is a huge difference between revision and repetition i.e., revision is not going through all the notes over and over again.

The specialized feature of revision is lessening of time in each and every attempt i.e., time consumed in revising the same content every time is less than the previous one. Just imagine a potential aspirant can revise the complete content of Physics syllabus in about two and a half hours in his 4th or 5th revision cycle.

Decrease in the time of revision is possible only when you have a proper analysis of 'what to revise' and 'what not to revise'. Such an analysis can be done on the basis of 'what you know' and 'what is whipped off from your memory after learning'. Every time when you go for only those parts which are whipped off, you find a lesser content to revise. This, in turn, certainly requires lesser time to reconcile.

Understand the concept and don't just mug. This is a big mistake made by many school going students till the mind maturity. Understanding the concept shows you the actual sweetness of the subject and makes you perceive even more of the subject with enthusiasm.

The difference between mugging and understanding is that, mugging is a memorising aspect while understanding is realsing the facts about the subject or topic with its related prior knowledge.

Use same notes or books or study material for all the revisions because the page of the book also strikes in memory during answering the questions asked.

There is no substitute for hard preparation and excitement and enthusiasm in revision.

Last but not least you are the best to know your situation, analyze it thoroughly and work out the best method for your revision. Think for yourself, you are mature enough to organize your own study plan. Use your discretion to judge what will work for you and what will not.

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@CLASS XI SYLLABUS

JEE Final Touch

Fast Track Revision

Some Basic Concepts of Chemistry

PROPERTIES OF MATTER AND THEIR MEASUREMENTS

Matter exist in three different forms such as solid, liquid and gas according to force of attraction between them. Physical and chemical properties of matter are quantitative in nature. To measure a quantitative property, various systems of measurement have been introduced, that vary according to the region. Hence, to standardise measurements International system of unit (SI system) was introduced which contains 7 basic units and 2 derived units. The following prefixes are also useful in representing a measurement.

Multiple	Prefix	Symbol	Submultiple	Prefix	Symbol
10	deca	da	10^{-1}	deci	d
10^{2}	hecto	h	10^{-2}	centi	c
10^{3}	kilo	k	10^{-3}	milli	m
10^{6}	mega	M	10^{-6}	micro	μ
10^{9}	giga	G	10^{-9}	nano	n
10^{12}	tera	T	10^{-12}	pico	p
10^{15}	peta	P	10^{-15}	femto	f
10^{18}	exa	E	10^{-18}	atto	a
10^{21}	zetta	Z	10^{-21}	zepto	z
10^{24}	yotta	Y	10^{-24}	yocto	y

Precision and Accuracy

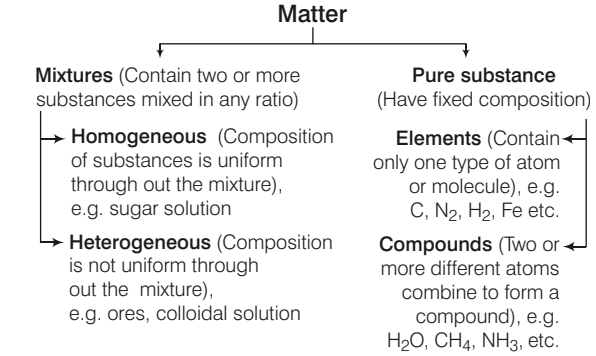
A measurement is said to be precise when the values of different measurements are close to each other. On the other hand, a measurement is said to be accurate when the average values of different measurements are close to the correct value. Uncertainty in measurement is expressed in terms of significant figure which is defined as the total number of digits in a quantity whose values are uncertain.

CHEMISTRY CONCENTRATE

SOME IMPORTANT UNIT CONVERSIONS

	Physical quantity	Units
1.	Mass	$1\,u = 1.66 \times 10^{-27}$ kg = 931.48 MeV 1 ton = 10^{3} kg = 10^{6} g = 10^{9} mg 1 metric ton = 10^{6} kg; 1 pound = 0.454 kg
2.	Volume	1 m^3 = 10^{3} L = 10^{6} mL = 10^{6} cm^3 1 L = 1 dm^3 = 10^{3} mL = 10^{-3} m^3
3.	Temperature	K = 273 + °C; °C = 5 / 9 (°F – 32)
4.	Pressure	1 atm ≈ 1.013×10^{5} Pa (N / m^2) ≈ 1013 bar ≈ 760 torr ≈ 760 mmHg ≈ 76 cm Hg
5.	Energy	1 eV = 1.602×10^{-19} J; 1 MeV = 10^{6} eV 1 cal ≈ 4.18 J; 1 J = 10^{7} erg

At macroscopic level matter can be classified into the following types



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Best Practice SHOTS

1. Which of the following statements are correct?

I. Matter is anything that has mass and occupies space.

II. Weight w is the force experienced by an object on earth and is equal to its mass m multiplied by acceleration due to gravity g, i.e. $w = mg$.

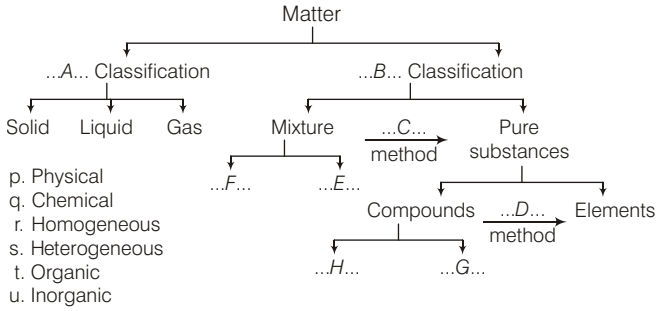
III. Energy and matter is neither created nor destroyed, but it can change its form, the total quantity of them in the universe is constant.

IV. Matter can be classified as physical forms and chemical forms.

V. Matter cannot be converted into energy and *vice-versa*.

(a) I, II and III *(b)* III, IV and V
(c) I, II, III and IV *(d)* All of these

2. Fill in the blanks (*A* to *H*).



p. Physical
q. Chemical
r. Homogeneous
s. Heterogeneous
t. Organic
u. Inorganic

Codes

	A	B	C	D	E	F	G	H
(a)	q	p	q	p	t	u	r	s
(b)	p	q	p	q	r	s	t	u
(c)	q	p	p	q	s	t	r	u
(d)	p	q	q	p	r	u	s	t

3. Match the following terms (Column (I)) with some related information (Column (II)).

Column I	Column II
A. Intensive *vs* extensive properties	p. Acidity *vs* colour
B. Chemical *vs* physical properties	q. Density *vs* volume
C. Isotropic *vs* anisotropic properties	r. Alloys *vs* soil
D. Homogeneous *vs* heterogeneous mixtures	s. Uniform *vs* non-uniform properties through the mixture

Codes

	A	B	C	D
(a)	q	p	r,s	r,s
(b)	r,s	p	q	r,s
(c)	p	q	p	r,s
(d)	q	q	r,s	p

4. Match the following quantities (Column I) with their SI base units (Column II).

Column I	Column II
A. Density	p. $JA^{-1}s^{-1}$
B. Pressure	q. AS
C. Electric charge	r. $kg\,m^{-1}s^{-2}$
D. Electric potential	s. Candela
E. Amount of substance	t. Kelvin
F. Luminous intensity	u. $kg\,m^{-3}$
G. Temperature	v. mol

Codes

	A	B	C	D	E	F	G
(a)	u	r	q	p	v	s	t
(b)	v	s	t	u	r	q	p
(c)	p	q	r	s	t	v	u
(d)	v	u	s	t	p	q	r

5. Select the incorrect statements. Choose the correct option.

I. $200\,lb = 90.7$ kg

II. 2 km = 345 miles

III. 0.8 carat = 0.1 kg

IV. $-20°C = 253.15\ K = -4°F$

(a) I and II *(b)* III and IV
(c) I and II *(d)* II and III

6. Match the following numbers (Column I) with the number of significant figures (Column II).

Column I	Column II
A. π	p. Infinite
B. Sum of $7.65 + 2.72 \times 10^{-2}$	q. Five
C. Product of $(7.6 \times 10^{7}) \times (3.8 \times 10^{-4})$	r. Four
D. 1.456×10^{1}	s. Three
E. 34000	t. Two

Codes

	A	B	C	D	E
(a)	s	q	q	r	t
(b)	p	q	q	r	t
(c)	p	s	r	r	q
(d)	s	s	r	q	q

7. Which of the following is homogeneous mixture?

(a) Dust *(b)* Bronze
(c) Pencil led *(d)* Antena rod

8. On the Reaumur scale (non longer used), water freezes at 0°R and boils at 80°R. What is the boiling point of mercury on this scale if it boils at 400°F?

(a) 828°R *(b)* 163.55°R
(c) 320°R *(d)* 500°R

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LAWS OF CHEMICAL COMBINATIONS, DALTON'S ATOMIC THEORY, MASSES OF CHEMICAL SPECIES

Laws of Chemical Combinations

Chemical reactions involving matter are governed by the following basic laws:

(a) **Law of conservation of mass** (Lavoisier, 1774) During a chemical reaction total mass of reactants is equal to the total mass of products or total mass remains constant during a chemical change.

(b) **Law of definite proportions** (Joseph Proust, 1799) When two or more elements combine to form a compound, they do so in a definite proportion by weight.

(c) **Law of multiple proportions** (Dalton, 1803) When two elements combine to form more than one compound, the masses of one element that combine with a fixed mass of other elements bear a simple ratio.

(d) **Gay Lussac's law of gaseous** volumes When different gases combine to form new compounds, the volumes of the reactants and those of gaseous products bear a simple ratio.

(e) **Law of reciprocal** (or equivalent) **proportions** (Richter, 1792) When two elements combine with fixed weight of third element then it is either the same or simple multiple ratio of weight of two elements which combine directly with each other.

(f) **Avogadro's law** At constant temperature and pressure, equal volumes of all gases contain equal number of molecules. The volume of one mole of a gas at STP is 22.4 L and it contains Avogadro's number of molecules ($N_A = 6.023 \times 10^{23}$).

Dalton's Atomic Theory

In 1803, Dalton proposed the first atomic theory having the following postulates:

(i) Matter consists of small indivisible particles (it is no more considered as indivisible after the discovery of proton, electron and neutrons) called atom, which take part in chemical reaction.

(ii) Atoms of same elements have identical properties and that of different elements have different properties.

(iii) Different atoms combine in a fixed ratio through chemical reaction to form compounds.

(iv) Atoms are neither created nor destroyed during a chemical reaction, rather they rearrange themselves to form new compounds.

Atomic Mass and Gram Atomic Mass (GAM)

The mass of one atom of any element is called atomic mass and is represented by amu or u. Atomic mass is a relative number. Atomic mass of one mole of an atom is called gram atomic mass and is represented in gram. Many atoms exist as different isotopes in different percentages. In such a case, average atomic mass is calculated.

Average atomic mass $= \dfrac{X_1A_1 + X_2A_2 + ...}{X_1 + X_2 + ...}$ where, X_1, X_2 ..... are percentage of relative abundance of atomic masses A_1, A_2 .... respectively.

Molecular and Molar Masses

Sum of atomic masses of all elements present in a molecule is called molecular mass. The mass of one mole of a molecule is called molar mass.

Equivalent Mass (*E*)

It is the number of parts of a substance that combines or displaces either directly or indirectly 1.008 parts by mass of hydrogen or 8 parts by mass of oxygen or 35.5 parts by mass of chlorine.

Equivalent mass of metal $= \dfrac{\text{Mass of metal}}{\text{Mass of } X \text{ displaced}} \times Y$

where, $X = H_2, O_2$ and Cl_2, $Y = 1.008$, 8 and 35.5

Formulae Related to Masses of Chemical Species

Atomic mass

- Atomic mass $= \dfrac{\text{Mass of one atom of } {}^{12}C}{12} \approx 1.66056 \times 10^{-21}$ kg
- Gram atomic mass = Atomic mass of 1 mole of an atom
- Average atomic mass $= \dfrac{X_1A_1 + X_2A_2 + \ldots}{X_1 + X_2 + \ldots}$ where X_1, X_2 ... are percentage of relative abundance of atomic masses A_1, A_2 ... respectively.

Molecular mass

- **Dulong and Petit's method** Average atomic mass × specific heat = 6.4
- **Volatile chloride method** Molecular weight of chloride (MCl_x)
  = 2 × vapour density = Atomic mass of M + x × atomic mass of Cl
- Atomic mass of a gas $= \dfrac{\text{Molecular mass}}{\text{Atomicity}}$
- Atomic mass = equivalent mass × valency

Equivalent mass

- Equivalent mass of metal $= \dfrac{\text{Mass of metal}}{\text{Mass of } X \text{ displaced}} \times Y$
  where, $X = H_2, O_2$ and Cl_2; $Y = 1.008$, 8 and 35.5
- $E_{\text{element}} = \dfrac{\text{Atomic mass of element}}{\text{Valence electrons of element}}$
- $E_{\text{ion}} = \dfrac{\text{Formula mass of ion}}{\text{Charge on ion}}$
- $E_{\text{salt}} = \dfrac{\text{Formula mass of salt}}{\text{Total positive or negative charge on cation or anion}}$
- $E_{\text{acid or base}} = \dfrac{\text{Molecular mass of acid or base}}{\text{Basicity or acidity}}$
- $E_{\text{oxidant or reductant}} = \dfrac{\text{Molecular mass of oxidant or reductant}}{\text{Number of electrons lost or gained by one molecule of oxidant or reductant}}$
- During metal displacement reaction, $\dfrac{\text{Mass of metal added}}{\text{Mass of metal displaced}} = \dfrac{E_{\text{metal added}}}{E_{\text{metal displaced}}}$

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Best Practice SHOTS

9. In an experiment, 2.4 g of iron oxide on reduction with hydrogen gave 1.68 g of iron. In another experiment, 2.9 g of iron oxide gave 2.09 g of iron on reduction. Which law is illustrated from the above data?
(a) Law of constant proportions *(b)* Law of multiple proportions
(c) Law of reciprocal proportions *(d)* Law of conservation of mass

10. Assuming that the results given below taken together illustrate the law of reciprocal proportions, calculate the masses of oxygen and hydrogen in 1.25 g of water.
I. 0.46 g of Mg produces 0.77 g of MgO.
II. 0.82 g of Mg liberates 760 mL of hydrogen at STP from an acid. (Weight of 1 mL of H_2 at STP = 0.00009 g)
(a) 0.8 g, 0.1 g *(b)* 1.11 g, 0.14 g
(c) 0.674 g, 0.083 g *(d)* 0.31g, 0.068 g

11. Which of the following statements is incorrect regarding Dalton's atomic theory?
(a) This theory could explain the laws of chemical combination except law of gaseous volumes
(b) It explains about the properties of atoms of same or different elements but does not explain why these elements combine to form molecules
(c) It does not explain why atoms of different elements have different masses, sizes, valencies, etc
(d) It could explain the nature of binding forces between the atoms of molecule responsible for the existence of matter in solids, liquids and gases

12. Match the following (Column I) which represents terms to the (Column II) representing their facts.

Column I	Column II
A. Average atomic mass	p. Sum of masses of all atoms in an ionic compound.
B. Gram molecular mass	q. Relative percentage occurrence of isotopes.
C. Formula mass	r. One mole of a substance in grams.
D. Molar mass	s. One mole of a gas at STP.
E. Molar volume	t. Sum of masses of all atoms in a compound expressed in grams.

Codes

	A	B	C	D	E		A	B	C	D	E
(a)	r	p	q	s	r	*(b)*	q	t	p	r	s
(c)	p	q	s	t	r	*(d)*	s	r	t	q	p

13. Carbon has three isotopes–carbon-12, carbon-13 and carbon-14. Whose percentage abundances are 98.92%, 1.108% and 2×10^{-10}% and atomic masses are 12, 13.00335 and 14.00317 u, respectively. What is the approximate average atomic mass of carbon?
(a) 12.1 u *(b)* 12.0 u *(c)* 12.9 u *(d)* 12.5 u

14. Which of the following statements is incorrect?
(a) The discovery of isotopes, isobars, artificial transmutation and non-stoichiometric compounds have lead to modification of Dalton's atomic theory
(b) Atoms are the components of molecules and the molecules are the components of elements or compounds
(c) Atomic mass of an element
$$= \frac{\text{Mass of one atom of the element}}{\text{Mass of one atom of carbon -12}}$$
(d) Number of molecules in 1 cm^3 or 1 mL of a gas at STP is known as Loschmidt number (2.68×10^{18} molecules/mL)

15. Match the items of (Column I) with (Column II).

Column I	Column II
A. 1.6 μg and CH_4	p. 3.408 ppm
B. 6.0 μ moles of Na_2SO_4 in 250 mL	q. 6.022×10^{16} molecules
C. Mass of one atom of $A = 3.9854 \times 10^{-23}$ g	r. Molecular mass = 64 g/mol
D. 16g gas occupies 5.6 L at STP	s. 2.5092×10^{22} atom/gram

Codes

	A	B	C	D		A	B	C	D
(a)	q	p	s	r	*(b)*	s	r	q	p
(c)	r	s	p	q	*(d)*	p	q	r	s

16. What is the exact atomic mass of the metal (with specific heat = 0.057 cal/g) if 4.51 g of the metal sulphate was formed on dissolving 2.0 g of metal in sulphuric acid?
(a) 114.72 *(b)* 113.84 *(c)* 112.5 *(d)* 108.63

17. Which of the following statement is incorrect regarding Cannizaro's method for the determination of atomic mass?
(a) Atomic mass of an element may be defined as the smallest mass of the element present in the molecular mass of any one of its compound
(b) Molecular masses of a number of compounds in which the element is present are determined
(c) Each compound is analysed, mass of the element is determined in molecular mass of each compound
(d) The highest mass of the element is taken as its atomic mass

18. What will be the atomic mass of chromium, when potassium chromate is found to contain 26.78% Cr and is found to be isomorphous to potassium sulphate?
(a) 39.1 *(b)* 52.00 *(c)* 142.2 *(d)* 73.22

19. The oxide of an element contains 32.33 per cent of the element and the vapour density of its chloride is 79. Calculate the atomic mass of the element.
(a) 15.28 *(b)* 38.2 *(c)* 6.767 *(d)* 24.2

20. Match the Column I items with the formula used in Column II using the information provided below and choose the correct option with correct codes.
I. 2.8 g hydrocarbon vapours at 127°C and 1 atm pressure occupies 1 L of volume.
II. Hydrogen to carbon ratio is 10.5:1 by mass in the hydrocarbon.

Column I	Column II
A. Molar mass	p. $\frac{\text{Mass of element}}{\text{Molar mass of compound}} \times 100$
B. Empirical formula	q. $pV = nRT$
C. Molecular formulae	r. $n \times$ empirical formula (n = integer)
D. Mass % of element	s. Atomic ratios and least whole number ratio

Codes

	A	B	C	D		A	B	C	D
(a)	q	s	r	p	*(b)*	p	r	q	s
(c)	q	r	p	s	*(d)*	r	q	s	p

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MOLE CONCEPT AND FORMULAE OF COMPOUNDS

Mole Concept

One mole is defined as the number of carbon atoms present in 12g of pure C^{12} isotope and is nearly equal to 6.023×10^{23}.

1 mole = 6.023×10^{23} atoms/molecules/ions

Number of moles

$$= \frac{\text{Mass of atom / molecule / ion}}{\text{Molar mass of atom / molecule / ion}}$$

$$= \frac{\text{Volume of gas (in L) at NTP}}{22.4}$$

$$= \frac{\text{Volume of gas (in mL)}}{22400}$$

$$= \frac{\text{Number of atoms / molecules / ions}}{6.023 \times 10^{23}}$$

Percentage Composition

The percentage of different elements present in a compound is called its percentage composition.

Empirical and Molecular Formulae

The simplest whole number ratio of different elements present in a compound is called empirical formula. The exact number of different atoms present in a molecule is called molecular formula.

Chemical Stoichiometry

It deals with the quantitative study of reactants and products in a chemical reaction. Problems in stoichiometry can be easily solved by applying laws of chemical combination.

(i) When the reaction is balanced

$C_2H_6(g)$ +	$\frac{7}{2}O_2(g)$	$\rightarrow 2CO_2(g)$ +	$3H_2O(g)$
1 molecule	$\frac{7}{2}$ molecules	2 molecules	3 molecules
1 mol	$\frac{7}{2}$ mol	2 mol	3 mol
30 g	112 g	88 g	54 g
1 vol	$\frac{7}{2}$ vol	2 vol	3 vol
22.4L	$\frac{7}{2} \times 22.4$ L	2×22.4 L	3×22.4 L (at STP)

(ii) If the reaction is not balanced, apply the concept that atoms in a chemical reaction are conserved, (principle of atomic conservation POAC).

POAC (Principle of Atomic Conservation)

If a reaction is given like

$$C_2H_6 + O_2 \rightarrow CO_2 + H_2O \text{ (unbalanced)}$$

Moles of C-atom in C_2H_6 = Moles of C-atom in CO_2

or $2 \times$ moles of $C_2H_6 = 1 \times$ moles of CO_2

Moles of H-atom in C_2H_6 = Moles of H-atom in H_2O

or $6 \times$ moles of $C_2H_6 = 2 \times$ moles of H_2O

Similarly, for O-atom

$$2 \times \text{moles of } O_2 = 2 \times \text{moles of } CO_2 + 1 \times \text{moles of } H_2O$$

We can calculate moles and masses of reactants and products easily by solving the above equations.

Limiting Reagent

During a chemical reaction, if a reactant is taken in lesser amount than the required amount, then it exhausted first and further reaction does not occur. Such a reactant is called the limiting reagent.

Note **While solving problems in stoichiometry**

(i) The limiting reagent is determined depending upon the condition given in the question.
But in the balanced chemical reaction, one reagent acts as limiting reagent.

(ii) The products formed will be in accordance with the limiting reagent.

(iii) Use volume of 1 mole of gas at STP as 22.4 L.

CHEMISTRY CONCENTRATE
RELATED TO STOICHIOMETRY

Follow the following steps while solving problems related to stoichiometry:

Step 1 Write down the reaction given in the question. If the reaction is not balanced apply principle of atomic conservation (POAC).

Step 2 Find out the type of relationship among reactants and products given, i.e.

(i) mole-mole relationship. (ii) mass-mass relationship.
(iii) mass-volume relationship. (iv) volume-volume relationship.

Step 3

(i) In mole-mole relationship, the reactants and products are given in terms of mole. Apply molar interpretation in the chemical reaction.

(ii) In mass-mass relationship, the reactants and products are given in terms of mass. Apply mass interpretation in the chemical reaction. This can also be solved by converting them into mole.

(iii) In mass-volume relationship, reactant is given in mass and is asked to calculate product in volume and *vice-versa*. In this case apply ideal gas equation, $pV = nRT = \frac{W}{M}RT$
to covert mass into volume.

(iv) In volume-volume relationship, both reactant and products are given in volume. Such problems can be solved by applying Avogadro's law and Gay-Lussac's law.

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Best Practice SHOTS

21. The vapour density of a mixture consisting of NO_2 and N_2O_4 is 38.3 at 26.7°C. Calculate the number of moles of NO_2 in 100g of the mixture. **[IIT JEE 1979]**

(a) 0.335 *(b)* 0.043 *(c)* 0.437 *(d)* 0.035

22. In the analysis of 0.5g sample of feldspar, a mixture of chloride of sodium and potassium is obtained, which weighs 0.1180 g, subsequent treatment of the mixed chlorides with silver nitrate gives 0.2451 g of silver chloride. What is the % of sodium oxide and potassium oxide in the sample? **[IIT JEE 1979]**

(a) 0.36%, 1.06% *(b)* 3.58%, 10.6%
(c) 10.6%, 3.58% *(d)* 1.06%, 0.36%

23. 5.00 mL of a gas containing only carbon and hydrogen was mixed with an excess of oxygen (30 mL) and the mixture exploded by means of electric spark. After explosion, the volume of the mixed gases was remaining 25 mL. On adding a concentrated solution of KOH, the volume further diminished to 15 mL, the residual gas being pure oxygen. All volumes have been reduced to NTP. Calculate the molecular formula of the hydrocarbon gas. **[IIT JEE 1979]**

(a) CH_4 *(b)* C_2H_4 *(c)* C_2H_6 *(d)* C_2H_2

24. An organic compound contains 49.30% carbon, 6.84% hydrogen and its vapour density is 73. Molecular formula of the compound is

(a) $C_3H_8O_2$ *(b)* $C_3H_{10}O_2$ *(c)* C_6H_9O *(d)* $C_6H_{10}O_4$

25. Calculate the percentage purity of NaCl sample, if 45.5% of Cl is found on analysis of impure sample of sodium chloride.

(a) 75 *(b)* 65 *(c)* 70 *(d)* 80

26. *A* is a binary compound of a univalent metal 1.422 g of *A* reacts completely with 0.321 g of sulphur in an evacuated and sealed tube to give 1.743 g of a white crystalline solid *B*, that forms a hydrated double salt, *C* with $Al_2(SO_4)_3$. Identify *A* **[IIT JEE 1994]**

(a) NaO_2 *(b)* K_2O *(c)* KO_2 *(d)* Na_2O

27. A solid mixture (5.0g) consisting of lead nitrate and sodium nitrate was heated below 600°C until the weight of the residue became constant. If the loss in weight was 28.0%, find the amount of lead nitrate and sodium nitrate in the mixture. **[IIT JEE 1990]**

(a) 3.6, 1.4 g *(b)* 3.3 g, 1.7 g
(c) 1.4 g, 3.6 g *(d)* 1.7 g, 3.3 g

CONCENTRATION TERMS AND STOICHIOMETRY

Concentration and composition of solution can be expressed by the following terms.

Molarity (*M*)

Number of moles of solute present in 1 L of a solution.

$$\text{So, } M = \frac{n_s}{V_{\text{sol (L)}}} = \frac{n_s \times 1000}{V_{\text{sol (mL)}}} = \frac{W_s \times 1000}{M_s \times V_{\text{sol (mL)}}}$$

where, n_s, W_s and M_s are moles, weight and molecular weight of solute respectively and V_{sol} is the volume of solution.

Note **Formality** (*F*) of a solution is practically same as the molarity. When molecular mass is replaced by formula mass, it is called formality.

Normality (*N*)

Number of gram-equivalents of solute present in 1L of a solution. So,

$$N = \frac{\text{Gram - equivalents of solute}}{V_{\text{sol (L)}}} = \frac{W_s}{E_s \times V_{\text{sol (L)}}} = \frac{W_s \times 1000}{E_s \times V_{\text{sol (mL)}}}$$

$$= \frac{W_s \times 1000}{\left(\frac{M_s}{n}\right) \times V_{\text{sol (mL)}}} = n \times \frac{W_s \times 1000}{M_s \times V_{\text{sol (mL)}}} = n \times M$$

Hence, normality = $n \times$ molarity where, n is the valency factor
Moles of solute = $M \times V_{(L)}$, Equivalents of solute = $N \times V_{(L)}$

Neutralisation Reaction

When acid and base are mixed, same equivalents of acid and base react with each other to form salt. Hence, $N_A V_A = N_B V_B$.

Mole Fraction (χ)

It is the ratio of moles of a particular component to the total number of moles present in a solution.

$$\chi_{\text{solute}} = \frac{n_{\text{solute}}}{n_{\text{solute}} + n_{\text{solvent}}} = \frac{\left(\frac{W}{M}\right)_{\text{solute}}}{\left(\frac{W}{M}\right)_{\text{solute}} + \left(\frac{W}{M}\right)_{\text{solvent}}}$$

$$\chi_{\text{solvent}} = \frac{n_{\text{solvent}}}{n_{\text{solute}} + n_{\text{solvent}}}$$

Molality (*m*)

It is the number of moles of solute present in 1 kg of solvent.

$$m = \frac{n_s}{W_{\text{solvent (kg)}}} = \frac{W_s}{M_s \times W_{\text{solvent (kg)}}} = \frac{W_s \times 1000}{M_s \times W_{\text{solvent (kg)}}}$$

Molarity and normality of a solution change with temperature, as they depend on volume. However molality (m) is independent of temperature, as it depend only on mass of solvent. Molality and mole fraction of solute and solvent are related by $m = \frac{\chi_{\text{solute}} \times 1000}{\chi_{\text{solvent}} \times M_{\text{solvent}}}$

where, M_{solvent} is the molecular mass of solvent.

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Formulae Related to Conversion of Concentration Terms & Concentrations in Terms of Percentages

If mole fraction of solute χ_{solute} and solvent $\chi_{solvent}$ are given and asked to calculate molarity (M). $M = \frac{\chi_{solute} \times 1000 \times \rho}{(\chi_{solute} \times M_{solute}) + (\chi_{solvent} \times M_{solvent})}$

If mole fraction is given and asked to find out molarity (m), $m = \frac{\chi_{solute} \times 1000}{(1 - \chi_{solute}) M_{solvent}}$

If molarity and density (ρ) of the solution is given and asked to find out molality, $\frac{1}{m} = \frac{\rho}{M} - \frac{M_{solute}}{1000}$

Concentration in terms of percentage (%)

% by weight $\frac{w}{w} = \frac{w_{solute}}{w_{solution}} \times 100$, % by volume $\frac{w}{V} = \frac{w_{solute}}{V_{solution}} \times 100$, % in parts per million $= \frac{w_{solute}}{w_{solution}} \times 100$

Weight percentage and molarity are related as: $M = \frac{\text{Weight percentage} \left(\frac{w}{w}\right) \times 10 \times \rho_{solution}}{M_{solute}}$

Percentage yield $= \frac{\text{Experimental yield}}{\text{Calculated yield (theoretical yield)}} \times 100$

- Relation between normality (N) and molarity (M) $\frac{\text{Normality}}{\text{Molarity}} = \frac{\text{Molecular weight}}{\text{Equivalent weight}} = $ Acidity/Basicity
- Dilution law, if normality or molarity and volume of solutin are changed from N_1, V_1 to N_2, V_2 then $N_1V_1 = N_2V_2$ (Normality equation)
  Similarly, $M_1V_1 = M_2V_2$ (Molarity equation)
- Suppose n_1 moles of reactant '1' react with n_2 moles of reactant '2' then $\frac{N_1V_1}{n_1} = \frac{N_2V_2}{n_2}$
- Suppose two solutions of the solute are mixed then normality of the resulting solution, $N = \frac{N_1V_1 + N_2V_2}{V_1 + V_2}$
- Volume of water added to get a solution of normality N_2 from V_1 mL volume of normality N_1 is $V_2 - V_1 = \left(\frac{N_1 - N_2}{N_2}\right) V_1$

Note ▪ Normality changes with temperature since it involves volume.
- When a solution is diluted x times, its normality also decreases by x times.
- Unit of normality = Gram equivalents litre.

Best Practice SHOTS

28. Molarity of a solution obtained by mixing 750 mL of 0.5 M HCl with 250 mL of 2 M HCl will be **[JEE Main 2013]**
(a) 0.875 M *(b)* 1.00 M *(c)* 1.75 M *(d)* 0.0975 M

29. Calculate the molarity of 10 mL sample of human urine having 5 mg of urea on analysis (Molar mass of urea = 60).
(a) 0.008 M *(b)* 0.005 M *(c)* 0.003 M *(d)* 0.08 M

30. Upon mixing 45.0 mL of 0.25 M lead nitrate solution with 25.0 mL of 0.1 M chromic sulphate solution, precipitation of lead sulphate takes place. Calculate the molar concentrations of reactant species left unreacted in the final solution **[IIT JEE 1993]**
(a) 0.054 M *(b)* 0.071 M *(c)* 0.075 M *(d)* 0.0375 M

31. 2.5 L of 0.5 NHCl and 7.5 L of 0.05 N $FeCl_3$ was added to 25 L of 0.1 NNaOH. Weight of Fe_2O_3 obtained is xg and normality of NaOH left in resultant solution is y N. The values of x and y are
(a) 10, 0.025 *(b)* 20, 0.05 *(c)* 40, 0.05 *(d)* 30, 0.15

32. What would be the molality of a solution obtained by mixing equal volumes of 30% by weight H_2SO_4 ($d = 1.218$ mL^{-1}) and 70% by weight H_2SO_4 ($d = 1.610$g/mL), if the resulting solution has density 1.425 g/mL?
(a) 4.2 m *(b)* 1.5 m *(c)* 7.61 m *(d)* 11.22 m

33. What volume of 95% H_2SO_4 by weight ($d = 1.85$g/mL) must be taken to prepare 100 mL of 15% solution of H_2SO_4 ($d = 1.10$ g/mL)?
(a) 9.4 mL *(b)* 11.0 mL *(c)* 18.5 mL *(d)* 4.9 mL

34. When ammonia was passed through 30 mL of 1 N H_2SO_4 solution, acid normality decreased to 0.2 N. What volume of ammonia gas at STP is used?
(a) 408.2 mL *(b)* 537.6 mL *(c)* 224.7 mL *(d)* 167.4 mL

35. In what ratio should you mix 0.2 M of $NaNO_3$ and 0.1 M of $Ca(NO_3)_2$ solution so that in resulting solution, the concentration of negative ions is 50% greater than the concentration of positive ions?
(a) 1 : 1 *(b)* 2 : 1 *(c)* 1 : 2 *(d)* 3 : 2

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{JEE FINAL TOUCH}

36. 100 mL of 0.1 MHCl, 100 mL of 0.2 M H_2SO_4 and 100 mL of 0.1 M H_3PO_4 are mixed together.

I. The final concentration of the solution is ...*A*... N.

II. If the solution is made of 1 L by adding water, then the final concentration of the solution is ...*B*... N.

(a) 0.23 and 0.06 *(b)* 0.26 and 0.08
(c) 0.36 and 0.02 *(d)* 0.26 and 0.03

37. 100 g solution of urea in water contain 40 g of urea (molar mass = 60 g/mol). What is the molality of urea solution?

(a) 9.09 m *(b)* 10.10 m *(c)* 11.11 m *(d)* 12.12 m

38. Fill in the blanks.

I. Aqueous urea solution is 20% by mass of solution and ...*A*...% by mass of solvent.

II. If the mole fraction of solute is 0.167, then the molality of aqueous solution is ...*B*... m.

III. 18 M H_2SO_4 aqueous solution (density of solution = 1.8 gL^{-1}) is ...*C*... molal.

IV. The molarity of K^+ in aqueous solution that contains 17.4 ppm of K_2SO_4 (174 g/mol) is ...*D*... M.

	A	B	C	D
(a)	30	10.10	400	1×10^{-4}
(b)	25	11.11	500	2×10^{-4}
(c)	20	1.11	300	3×10^{-4}
(d)	15	1.01	200	4×10^{-4}

39. Match the following species undergoing chemical change in (Column I) with the *n*-factor in (Column II).

$$n\text{-factor, } n = \frac{\text{Molecular weight}}{\text{Equivalent weight}}$$

Column I		Column II	
A.	As_2O_3 is oxidised in basic medium.	p.	$n = 8$
B.	Br_2 undergoes disproportionation in basic medium.	q.	$n = \frac{3}{7}$
C.	H_2O_2 undergoes disproportionation in acidic medium.	r.	$n = 1$
D.	1 mole of $K_2Cr_2O_7$ reacts with 14 moles of HCl.	s.	$n = \frac{10}{6}$
E.	Salt, $K_2SO_4\times Al_2(SO_4)_3\times 24H_2O$	t.	$n = 28$

Codes

	A	B	C	D	E		A	B	C	D	E
(a)	p	q	r	s	t	*(b)*	q	t	q	p	r
(c)	r	p	q	t	s	*(d)*	t	s	r	q	p

Answers

1. (c)	**2.** (b)	**3.** (a)	**4.** (a)	**5.** (d)	**6.** (c)	**7.** (b)	**8.** (b)	**9.** (a)	**10.** (b)
11. (d)	**12.** (b)	**13.** (b)	**14.** (c)	**15.** (a)	**16.** (a)	**17.** (d)	**18.** (b)	**19.** (a)	**20.** (a)
21. (c)	**22.** (b)	**23.** (b)	**24.** (d)	**25.** (a)	**26.** (c)	**27.** (b)	**28.** (a)	**29.** (b)	**30.** (a)
31. (a)	**32.** (d)	**33.** (a)	**34.** (b)	**35.** (c)	**36.** (b)	**37.** (c)	**38.** (b)	**39.** (d)	

MASTER STROKES

1. Aluminium and sulphuric acid react according to the reaction :

$$2Al(s) + 3H_2SO_4(aq) \rightarrow Al_2(SO_4)_3(aq) + 3H_2(g)$$

If 0.5 mole Al are added to H_2SO_4 solution containing 0.2 mole H_2SO_4 how many moles of H_2 are produced?

(a) 0.2 *(b)* 0.6 *(c)* 0.4 *(d)* 0.6

2. 1.0L of mixture of CO and CO_2 is taken. This mixture is passed through a tube containing red hot charcoal. The volume now becomes 1.6 L, the volumes are measured under the same conditions. Find the composition of mixture by volume.

(a) 55% CO, 45% CO_2 *(b)* 50% CO, 50% CO_2
(c) 60% CO, 40% CO_2 *(d)* 40% CO, 60% CO_2

3. A plant virus is found to consist of uniform cylindrical particles of 150Å in diameter and 5000 Å long. The specific volume of the virus is 0.75 cm^3/g. If the virus is considered to be a single particle, find its molar mass.

(a) 70.92×10^6 g *(b)* 1.2×10^6 g
(c) 8.8×10^6 g *(d)* 7.5×10^6 g

4. Which of the following statements illustrate the law of multiple proportion?

(a) 3.47 g of $BaCl_2$ reacts with 2.36 g of Na_2SO_4 to give 3.88 g $BaSO_4$ and 1.95 g NaCl

(b) Hydrogen sulphide contains 5.89% hydrogen, water contains 11.1% hydrogen and sulphur dioxide contains 50% oxygen

(c) An element forms two oxides *XO* and XO_2 containing 50% and 60% oxygen, respectively. The ratio of masses of oxygen which combines with 1g of element is 2:3

(d) 20 mL ammonia gives 10 volumes of N_2 and 30 volumes of H_2 at constant temperature and pressure

5. Match the activity of HNO_3 in (Column I) with the equivalent weights of HNO_3 in (Column II).

Column I		Column II	
A.	As an acid	p.	63 g
B.	Conc. HNO_3 as an oxidising agent (OA)	q.	21 g
C.	Dil. HNO_3 (OA)	r.	10.5 g
D.	Cold dil.HNO_3	s.	7.875 g
E.	Very dil. HNO_3 (OA)		

Codes

	A	B	C	D	E		A	B	C	D	E
(a)	q	r	s	t	p	*(b)*	s	r	q	r	p
(c)	p	p	q	r	s	*(d)*	r	q	r	p	s

6. *n*-butane is produced by monobromination of ethane followed by Wurtz reaction. Calculate the volume of ethane at NTP required to produce 55 g *n*-butane, if the bromination takes place with 90% yield and the Wurtz reaction with 85% yield.

(a) 45.45 L *(b)* 50.05 L *(c)* 55.50 L *(d)* 60.10 L

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7. Match the following property of elements in Column I with the element in Column II.

Column I	Column II
A. Metal in liquid state	p. Bromine
B. Non-metal in liquid state	q. Hydrogen
C. Metal with low density	r. Mercury
D. Non-metal as good conductor of electricity	s. Lithium

Codes

	A	B	C	D		A	B	C	D
(a)	p	q	r	s	*(b)*	r	s	q	p
(c)	s	r	q	p	*(d)*	r	p	s	q

8. Match the following properties of one of the components of a mixture in (Column I) that is used by separation method in (Column II).

Column I	Column II
A. Insolubility of a solid in solvent	p. Magnetic separation
B. Solid component vaporises	q. Solvent extraction
C. Liquid component vaporises	r. Distillation
D. Magnetic property	s. Sublimation
E. Preferential solubility in a particular solvent	t. Filtration

	A	B	C	D	E		A	B	C	D	E
(a)	p	q	r	s	t	*(b)*	t	s	r	q	p
(c)	t	s	q	r	q	*(d)*	r	p	q	s	t

9. Match the following reactions in (ColumnI) with their type in (Column II).

Column I	Column II
A. $KOH + HCl \rightarrow KCl + H_2O$	p. Combination
B. $NH_4CNO \rightleftharpoons NH_2CONH_2$	q. Substitution
C. $C_2H_4 + HBr \rightleftharpoons C_2H_5Br$	r. Addition
D. $SO_2 + H_2O \rightleftharpoons H_2SO_3$	s. Internal rearrangement
E. $Zn + 2HCl \rightleftharpoons ZnCl_2 + H_2$	t. Double decomposition

	A	B	C	D	E		A	B	C	D	E
(a)	t	s	r	p	q	*(b)*	q	r	p	s	t
(c)	s	t	q	r	p	*(d)*	r	q	p	t	s

10. 50 mL of 0.2 M HCl, 50 mL of 0.2 N H_2SO_4 and 200 mL of 0.2 M $Ba(OH)_2$ are mixed together and the volume is made to 1 L by adding H_2O. What is the final concentration of the solution and the nature of the final solution, acidic, basic or neutral?

(a) 0.06 N, basic *(b)* 0.02 N, acidic
(c) 0.04 N, neutral *(d)* None of these

Answers

1. (c) **2.** (d) **3.** (a) **4.** (c) **5.** (c) **6.** (c) **7.** (d) **8.** (b) **9.** (a) **10.** (a)

Atomic Structure

SUBATOMIC PARTICLES, ATOMIC MODELS, DUAL NATURE OF ELECTROMAGNETIC RADIATION AND PHOTOELECTRIC EFFECT

- Dalton's atomic model was unable to explain various properties of matter like carrier of charge, heat etc. It also failed to explain internal structure of an atom. This lead to the discovery of subatomic particles like electron, proton, neutron, positron, etc.
- The details about some of the important subatomic particles are given in the table below

Name and symbol	Absolute charge (c)	Relative charge	Mass (gram)	Mass (Mev/C^2)	Discoverer
Electron (e)	-1.602×10^{-19}	−1	9.1×10^{-28}	0.511	JJ Thomson
Proton (p)	$+1.602 \times 10^{-19}$	+1	1.6726×10^{-24}	938.5	Rutherford
Neutron (n)	0	0	1.6749×10^{-24}	940	Chadwick
Positron (B^+/e^+) (anti-electron)	$+1.602 \times 10^{-19}$	+1	9.1×10^{-28}	0.511	D Anderson
Anti-proton ($\bar{p}$)	-1.602×10^{-19}	−1	1.6726×10^{-24}	938.5	Emilio & Owen

Rutherford's Experiment

Rutherford passed energetic α-particles through a very thin (10^{-7} m) gold foil and concluded the following:

(i) Most of the α-particles (≈99%) passed undeflected, concluding that most of the space in an atom is empty.

(ii) The rest of the α-particles were deflected by small angles, and only a very few α-particles retraced the path (θ = 180°). This concluded that the positive charge and whole mass of atom is concentrated at a small place called nucleus.

Radius of an atom $\approx 10^{-10}$ m & nucleus $\approx 10^{-15}$ m

$$\frac{\text{Volume of nucleus}}{\text{Volume of atom}} \approx \frac{10^{-45}}{10^{-30}} \approx 10^{-15}$$

(iii) Electrons move in circular paths called orbits and electrons and nucleus are held together by electrostatic force of attraction.

Quarks

- The research on subatomic particles over the years has shown that protons and neutrons are themselves composed of still smaller particles named as quarks.
- A quark is an elementary particle and a fundamental constituent of matter. Quarks can combine to form composite particles called hardons. The most stable hardons are protons and neutrons.
- Quarks has various intrinsic properties including electric charge, mass, colour, charge and spin.
- The existence of quarks has let us understand how atomic nucleus stays together inspite of the presence of positively charged particles in close proximity.

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CHEMISTRY CONCENTRATE

TERMS RELATED TO ATOM

Atomic number (Z)	Equal to the number of protons (or electrons) in a neutral atom.
Mass number (A)	Number of protons (Z) + number of neutrons (N); ($A = Z + N$)
Isotopes	Atoms of same element having different mass number, e.g. $_6C^{12}$, $_6C^{14}$.
Isobars	Atoms of different elements having same mass number, e.g. $_6C^{14}$, $_7N^{14}$.
Isotones	Atoms of different elements having same number of neutrons, e.g. $_{19}K^{39}$, $_{20}Ca^{40}$. $_{16}S^{36}$.
Isoelectronic	Species having same number of electrons, e.g. K^+, Ca^{2+}, Ar, Cl^-
Isodiaphers	Different atoms having same neutron to proton difference (neutron excess), e.g. $_{92}U^{238}$, $_{90}Th^{234}$, both have ($N - Z$) equal to 54.
Isosteres	Species having same number of atoms and electrons are isosteres, e.g. N_2 and CO.

Charge by mass ratio (e/m) It is the ratio of charge to the mass of charged particles like electron, proton, etc. e/m ratio for electron was first measured by JJ Thomson.

(i) For electron, (e/m) ratio

$$= \frac{1.602 \times 10^{-19}\,C}{9.1 \times 10^{-28}\,g} = 1.76 \times 10^{8}\ Cg^{-1}$$

(ii) For proton, (e/m) ratio = $9.58 \times 10^{4}\ Cg^{-1}$

According to the classical electrodynamics, two particles with same (e/m) ratio trace the same path in vacuum, when same electric and magnetic field are applied. Recently, mass spectrometer is used to determine (e/m) ratio.

Charge of electron was calculated by RA Millikan, by considering the downward movement of a charged oil drop under the influence of electric field. This process is called Millikan's oil drop method.

Drawbacks of Rutherford's Model

(i) It failed to explain the stability of atom.
(ii) It fails to explain how the electrons are configured around the nucleus and the energy of electron.
(iii) It could not explain atomic spectra of H-atom and discontinuous spectrum.

Developments Leading to the Bohr's Atomic Model

(a) Dual Nature of Electromagnetic Radiation (EMR)

EMR possesses both wave as well as particle nature.

(i) **Wave nature** Electromagnetic radiations are transverse waves propagate in vacuum with the speed of light ($c \approx 3 \times 10^8\ ms^{-1}$). Different types of electromagnetic radiations exist which differ from each other by wavelength (or frequency, $\nu = c/\lambda$). When these radiations are arranged in the order of their wavelengths (or frequencies), these constitute electromagnetic spectrum as shown in the table below.

Different Electromagnetic Radiations

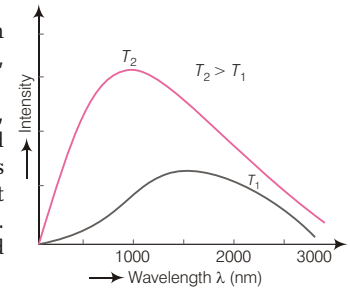
Name	Wavelength (Å)	Frequency (Hz)	Generation Source
Radiowave	$3 \times 10^{14} - 3 \times 10^{7}$	$1 \times 10^{5} - 1 \times 10^{9}$	Alternating current of high frequency.
Microwave	$3 \times 10^{7} - 6 \times 10^{6}$	$1 \times 10^{9} - 5 \times 10^{11}$	Klystron tube
Infrared (IR) waves	$6 \times 10^{6} - 7600$	$5 \times 10^{11} - 3.95 \times 10^{14}$	Incandescent objects
Visible	7600 – 3800	$3.95 \times 10^{14} - 7.9 \times 10^{14}$	Electric bulb, Sun rays
Ultraviolet wave (UV)	3800 – 150	$7.9 \times 10^{14} - 2 \times 10^{16}$	Sun rays, mercury vapour
X-rays	150 – 0.1	$2 \times 10^{16} - 3 \times 10^{19}$	Cathode rays striking metal plate
γ-rays	0.1 – 0.01	$3 \times 10^{19} - 3 \times 10^{20}$	Radioactive decay
Cosmic rays	0.01 – zero	3×10^{20} – infinity	Outer space

(ii) **Particle nature** Wave nature of electromagnetic radiations is unable to explain the properties of electromagnetic radiations like black body radiation, photoelectric effect, line spectra of hydrogen atom, etc., which can be explained by the particle nature of electromagnetic radiations. Radiations by a black body (an ideal body that emits and absorbs radiations of all frequencies) can be explained by Planck's quantum theory.

(b) Quantised Electronic Energy Levels

- **Planck's quantum theory** Atoms emit or absorb energy in discrete quantity called quanta. Energy associated with a quanta is given by $E = h\nu = \frac{hc}{\lambda}$ $[\because \nu = c/\lambda]$

  where, h is Planck's constant and is equal to 6.626×10^{-34} Js. ν = frequency of emitted radiation
- Energy is always emitted in integral multiple of $h\nu$ (i.e. $h\nu$, $2h\nu$, $3h\nu$...).
- When a black body is heated, the frequency of emitted radiation increases as temperature increases, i.e. it only depends on temperature. This can be better understood by the graph.



Photoelectric Effect

When a beam of light strikes a metal surface, it ejects electrons. This phenomenon is called photoelectric effect, and explained by Albert Einstein by using Planck's quantum theory. When a light of frequency (ν) more than threshold frequency (ν_0), strikes a metal surface, $h\nu_0$ amount of energy is used in removing the electron from metal surface and the rest of the energy ($h\nu - h\nu_0$) is used in moving the electron with velocity v.

Hence, $$\frac{1}{2} m_e v^2 = h\nu - h\nu_0 = h(\nu - \nu_0)$$

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Photoelectric Effect in Automatic Doors

- You may be seen many elevators and garage doors systems which open up automatically, when a person comes near them.
- These systems use a beam of light and a photoelectric device known as a photocell.
- As long as the beam of light strikes the photocell, the photoelectric effect generates enough ejected electrons to produce α detectable electric current.
- When the light beam is blocked by a person, the electric current is interrupted and the doors are signaled to open.

Spectrum

The arrangement of radiations in the order of their wavelengths (or frequencies) is called spectrum.

A spectrum is said to be **emission spectrum**, when radiations are emitted due to the supply of energy. When a continuous spectrum passed through a matter, it absorbs radiation of a particular wavelength (or frequency) and become excited. This missing wavelength leaves a dark space in continuous spectrum. This type of spectrum is called **absorption spectrum**. A spectrum can be further classified into two categories such as

(a) **Continuous or band spectrum** A spectrum in which there is no sharp boundary between two different radiations, e.g. the spectrum produced due to dispersion of white light, where different colours merge with each other.

(b) **Discontinuous or line spectrum** A spectrum in which radiations of a particular wavelength are separated from each other through sharp boundaries, i.e. in discontinuous spectrum, only radiations of some particular wavelengths are produced.

Note Discontinuous (line) spectra are produced by gaseous atoms in excited state, e.g. hydrogen spectra. Each atom has a unique line spectrum. This concept is used in identifying unknown atoms in chemical reactions by spectroscopic method.

Best Practice SHOTS

1. Electrical discharge through the gases in a cathode ray tube is observed only at
(a) very low pressure and very low voltage
(b) very high pressure and very high voltage
(c) very high pressure and very low voltage
(d) very low pressure and very high voltage

2. Which of the following statements are correct regarding the properties of cathode rays?
I. When cathode rays are focused on a thin metal foil, it gets heated upto incandescence.
II. These consist of material particles and travels in straight lines.
III. These do not get deflected in presence of electric and magnetic field.
IV. Charge to mass ratio (e/m) of the particles in the cathode is dependent on the nature of the gas taken in the discharge tube and the nature of the cathode.
Choose the appropriate option.
(a) I and II *(b)* III and IV *(c)* I and III *(d)* II and IV

3. Which of the following statements are incorrect?
I. Canal rays are simply charged gaseous ions.
II. Charge to mass ratio of these particles is found to depend on the gas from which these originate.
III. Some of the positively charged particles carry a multiple of fundamental unit of electrical charge.
IV. Behaviour of canal rays in the electrical or magnetic field is opposite to that observed for cathode rays or electron. Choose the correct option.
(a) I and II *(b)* I, II and III
(c) I, II, III and IV *(d)* None of these

4. Consider the following facts regarding α, β and γ-rays.
I. α-rays consist of high energy particles carrying two units of positive charge and four units of atomic mass.
II. β-rays are negatively charged particles similar to electrons.
III. γ-rays are high energy radiation like X-rays, are neutral in nature and do not consist of particles.
IV. Penetrating power : α-rays > β-rays > γ-rays.
Choose the correct statements mark the right option.
(a) I and II *(b)* I, II and III
(c) I, II, III and IV *(d)* None of these

5. Which of the following statements would you consider as the observation made by Rutherford in α-particle scattering experiment?
I. Whenever α-particle struck the fluorescent screen, a tiny flash of light was produced at that point.
II. Most of the α-particles (~99%) passed through the gold foil undeflected.
III. A small fraction of α-particles were deflected by small angles.
IV. Very few α-particles bounced back, that is they were deflected by nearly 180°.
Choose the correct option.
(a) I and II *(b)* III and IV *(c)* I, II and III *(d)* II, III and IV

6. Through the observation made by Rutherford, he drew the following conclusions regarding the structure of atom. These are

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I. Most of the space in an atom is empty.
II. Nucleus consists of positively charged protons and its size is 10^5 times smaller than that of atom.
III. The model of atom resembles to the solar system. (nucleus → sun; electrons → planets).
IV. The centrifugal force arising due to the high speed of an electron balances the coulombic force of attraction of the nucleus and the electron remains in its path. Choose the correct statements.

(a) I, II and III *(b)* II, III and IV
(c) All of these *(d)* None of these

7. The stability of nucleus depends on the ratio *n/p* (number of neutrons to number of protons). Which of the following statements regarding nuclear stability is incorrect?

(a) If $n/p = 1$, nucleus is found to be very stable
(b) with increase in atomic number, number of neutrons goes on increasing in comparison to the number of protons
(c) Upto atomic number 40, $n/p = 1$
(d) When the ratio of *n/p* is more than 1.5, nucleus becomes constable and radioactive (i.e. at. no. > 83)

8. Match the following items (Column I) with items of (Column II) (Rutherford's scattering equation).

Column I	Column II
A. Distance of closest approach.	p. $N = K_2 / [\sin^4(\theta/2)]$
B. Kinetic energy of α-particles.	q. $N = K_3 (Ze)^2$
C. Scattering angle 'θ'.	r. $N = K_1 / [(1/2)mv^2]^2$
D. Nuclear charge	s. $r_0 = \frac{1}{4\pi\varepsilon_0}\frac{2Ze^2}{E_K}$

Codes

	A	B	C	D		A	B	C	D
(a)	p	q	r	s	*(b)*	s	r	p	q
(c)	s	r	q	p	*(d)*	p	q	s	r

9. Which of the following shows an increasing value of *e/m*?

(a) $n < \alpha < p < e$ *(b)* $n < p < \alpha < e$
(c) $n < p < e < \alpha$ *(d)* $p < n < \alpha < e$

10. In two elements ${}_{Z_1}A^{M_1}$ and ${}_{Z_2}A^{M_2}$, $M_1 \neq M_2$ and $Z_1 \neq Z_2$ but $M_1 - Z_1 = M_2 - Z_2$. These elements are

(a) isotonic *(b)* isobaric *(c)* isotopic *(d)* isoprotonic

11. Calculate the density of fluorine nucleus supposing that the shape of the nucleus is spherical and its radius is 5×10^{-13} cm (Mass of $F = 19$u)

(a) 9×10^{13} g/cm^3 *(b)* 6×10^{13} g/cm^3
(c) 6×10^{7} g/cm^3 *(d)* 9×10^{7} g/cm^3

12. Determine the percentage of F in a mixture sample F and Cl atoms, when removal of an electron from each atom of the sample absorbs energy equal to 284 kJ, while an addition of an electron to each atom of the mixture releases energy of 68.8 kJ.
(Given, $EA_F = 5.53 \times 10^{-22}$ kJ, $EA_{Cl} = 5.78 \times 10^{-22}$ kJ, $IE_F = 27.91 \times 10^{-22}$ kJ and $IE_{Cl} = 20.77 \times 10^{-22}$ kJ)

(a) 62.19% *(b)* 37.81% *(c)* 20.77% *(d)* 27.91%

13. Calculate the velocity of electron ejected from a platinum surface when radiation of 200 nm falls on it. The work function of platinum is 5 eV. (1 eV $= 1.6 \times 10^{-19}$ J)

(a) 6.54×10^5 m/s *(b)* 6.54×10^4 m/s
(c) 6.54×10^8 m/s *(d)* 6.54×10^6 m/s

14. Particle nature of electromagnetic radiation is not observed in which of the following phenomenon?

(a) Black body radiation and photoelectric effect
(b) Interference and diffraction
(c) Variation of heat capacity of solids as a function of temperature
(d) Line spectra of atoms

BOHR MODEL, DUAL NATURE OF MATTER AND HEISENBERG'S UNCERTAINTY PRINCIPLE

Bohr's Atomic Model

Bohr proposed the following postulates to remove the drawbacks in Rutherford's atomic model

(i) Electrons move around the nucleus in circular paths called orbits, each having a particular amount of energy. The energy of orbit increases as the distance of orbit from nucleus increases.
(ii) An electron does not radiate energy as long as it revolves in a particular orbit. It makes a transition from one orbit to another, when it emits or absorbs energy.
(iii) The angular momentum associated with an orbit is integral multiple of $h/2\pi$. So, $mvr = nh/2\pi$
(iv) During the revolution in an orbit, the necessary centripetal force is provided by the electrostatic force of attraction between electron and nucleus.

So, $\frac{m_e v^2}{r} = \frac{KZe^2}{r^2}$ where, $k = \frac{1}{4\pi\varepsilon_0} = 9 \times 10^9$ Nm^{2}C^{-2}

Property	Formulae	Numerical value
Radius Bohr's orbit(*r*)	$r_n = \frac{n^2h^2}{4\pi^2 mKZe^2}$	$r = 0.529\left(\frac{n^2}{Z}\right)$ Å
Energy of orbits (a) Kinetic energy (KE)	$KE = \frac{2\pi^2 mK^2Z^2e^4}{n^2h^2}$	$KE = 13.6\left(\frac{Z^2}{n^2}\right)$ eV atom^{-1} $= +21.8 \times 10^{-19}\left(\frac{Z^2}{n^2}\right)$ J atom^{-1}
(b) Potential energy (PE)	$PE = \frac{-4\pi^2 mK^2Z^2e^4}{n^2h^2}$	$PE = -27.2\left(\frac{Z^2}{n^2}\right)$ eV atom^{-1}
(c) Total energy (E_n = KE + PE)	$E_n = \frac{-2\pi^2 mK^2Z^2e^4}{n^2h^2}$	$E_n = -13.6\left(\frac{Z^2}{n^2}\right)$ eV atom^{-1} $= -21.8 \times 10^{-19}\left(\frac{Z^2}{n^2}\right)$ Jatom

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Property	Formulae	Numerical value

Energy of different orbits of H-atom (in eV)

1	2	3	4	∞
–13.6	–3.4	–1.51	– 0.85	∞

→ Increasing order

Velocity of electron (v)	$v_n = \frac{2\pi K Ze^2}{nh}$	$v_n = 2.188 \times 10^6 \left(\frac{Z}{n}\right)$ m s^{-1}
Time period of revolution of electron (T)	$T_n = \frac{n^3h^3}{4\pi^2 mK^2Z^2e^4}$ $\left(T_n = \frac{2\pi r_n}{v_n}\right)$	$T_n = 1.5 \times 10^{-16} \left(\frac{n^3}{Z^2}\right)$ s
Orbital frequency $\left(\nu = \frac{1}{T_n}\right)$	$\nu = \frac{1}{T_n} = \frac{4\pi^2 mK^2Z^2e^4}{n^3h^3}$	$\nu = \frac{1}{T_n} = 6.66 \times 10^{15} \left(\frac{Z^2}{n^3}\right)$ s^{-1}

Line Spectrum of Hydrogen

When H_2 gas is subjected to electric discharge, the H_2 molecules dissociate and become excited. The excited atoms radiate electromagnetic radiation of definite frequency in UV, visible and infrared region of electromagnetic spectrum.

- Balmer first observed line spectrum of hydrogen in visible region.
- Rydberg gave the following formulae to calculate the wave number $\left(\frac{1}{\lambda}\right)$ associated with electromagnetic radiation emitted by different atoms $\nu = \frac{1}{\lambda} = R_H Z^2 \left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$, $n_1 < n_2$

  where, $R_H = \frac{2\pi^2 m_e e^4}{ch^3} = 109677 \text{ cm}^{-1}$

  $= 10967700 \text{ m}^{-1}$ is called Rydberg's constant.

  Z = atomic number

  n_1 and n_2 are lower and higher orbit respectively ($n_1 < n_2$).

Subsequently, the following different types of line spectrum of hydrogen were discovered.

Series of lines	n_1	n_2	Spectral region	Wavelength range
Lyman series	$n_1 = 1$	$n_2 = 2, 3, 4, \ldots \infty$	UV light < 4000 Å	$1/R_H - 4/3\ R_H$
Balmer series	$n_1 = 2$	$n_2 = 3, 4, 5, \ldots \infty$	Visible 4000-7000 Å	$4/R_H - 36/5\ R_H$
Paschen series	$n_1 = 3$	$n_2 = 4, 5, 6, \ldots \infty$	Near infrared > 7000 Å	$9/R_H - 144/7\ R_H$
Brackett series	$n_1 = 4$	$n_2 = 5, 6, 7, \ldots \infty$	Infrared > 7000 Å	$16/R_H - 400/9\ R_H$
Pfund series	$n_1 = 5$	$n_2 = 6, 7, 8, \ldots, \infty$	Far infrared > 7000 Å	$25/R_H - 900/11\ R_H$
Humphrey series	$n_1 = 6$	$n_2 = 7, 8, 9, \ldots \infty$	Far infrared > 7000 Å	$36/R_H - 1764/13\ R_H$

- Maximum number of spectral lines that can be obtained from ground state ($n = 1$) to nth excited state is $\frac{n(n-1)}{2}$.
- Maximum number of spectral lines that can be obtained from n_1th orbit to n_2th orbit is $\frac{(n_2 - n_1 + 1)(n_2 - n_1)}{2}$ e.g. for $n = 1$ to $n = 4$, maximum number of spectral lines that can be obtained is 6.

Limitations of Bohr's Model

(i) Applicable to atoms/ions having single electron.
(ii) Unable to explain Zeeman and Stark effect (splitting of spectral lines in the presence of static magnetic field and an external electric field respectively).
(iii) Unable to explain shape of atom in three dimensional space.
(iv) Unable to explain dual nature of electron. Also it does not follow Heisenberg's uncertainty principle.

Dual Nature of Matter

de-Broglie suggested that like electromagnetic radiation, matter also possesses dual nature. Hence, like photon, electron has also both momentum and wavelength. This can be explained by Planck's quantum theory and Einstein's mass-energy equation ($E = mc^2$). The wavelength and momentum associated with matter is given by

$$\lambda = \frac{h}{mc} = \frac{h}{P} = \frac{h}{\sqrt{2mE}} \text{ (de-Broglie equation)}$$

When a charged particle(q) is accelerated by a potential V, the kinetic energy and wavelength of charged particle is given by $KE = \frac{1}{2}mv^2 = qV$ or $P = \sqrt{2qVm}$ or $\lambda = \frac{h}{\sqrt{2qVm}}$

where, q and m are charge and mass of charged particle respectively. For a gas molecule, $\lambda = \frac{h}{mv}$.

Heisenberg's uncertainty principle According to this principle, the exact position and velocity (momentum) of subatomic particles cannot be determined simultaneously, i.e. there must be a minimum error of $\frac{h}{4\pi}$, which is exactly opposite of Bohr's atomic theory. $\Delta P \times \Delta x \geq \frac{h}{4\pi}$

or $\Delta v \times \Delta x \geq \frac{h}{4\pi m}$ or $\Delta E \times \Delta t \geq \frac{h}{4\pi}$

Best Practice SHOTS

15. A photon of frequency, ν causes photoelectric emission from a surface with threshold fequency ν_0.

The de-Broglie wavelength (λ) of photoelectron emitted is given by

(a) $\Delta n = \frac{h}{2m\lambda}$ (b) $\Delta n = \frac{h}{\lambda}$

(c) $\left[\frac{1}{\nu_0} - \frac{1}{\nu}\right] = \frac{mc^2}{n}$ (d) $\lambda = \sqrt{\frac{h}{2m\Delta v}}$

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16. In the Balmer series of atomic spectra of hydrogen, there is a line corresponding to wavelength 4344 Å. Calculate the number of higher orbits from which the electron drops to generate other lines ($R \times c = 3.289 \times 10^{15}$)
(a) 3 *(b)* 4 *(c)* 5 *(d)* 6

17. Positronium consists of an electron and a positron (same mass, opposite charge) orbiting around their common centre of mass. The spectrum is, therefore expected to be hydrogen like, the difference arising from the mass difference. Calculate the wave number of third line of Balmer series of positronium.
(a) 7620.6 cm^{-1} *(b)* 10288 cm^{-1}
(c) 11522 cm^{-1} *(d)* 54868 cm^{-1}

18. Which of the following statements is correct for a H like species?
(a) The energy gap between the consecutive energy orbits decreases as the value of '*n*' increases
(b) The longest wavelength in any spectral series corresponds to α-line in that series
(c) Each spectral series is bounded by minimum and maximum wavelengths and the range follows a continuous distribution as given by Bohr's theory
(d) KE of the electron decreases, whereas the PE increases as the value of '*n*' increases

19. The energy of the electron in a hydrogen atom has a negative sign for H-atom because
(a) the energy of the electron in the atom is lower than the energy of a free electron at rest
(b) a free electron at rest is electron that is infinitely far away from the nucleus
(c) the energy values assigned to free electron at rest is zero
(d) All of the above

20. The main postulates of Bohr's theory are as follows:
I. The electron in the hydrogen atom revolves around the nucleus in a circular path of fixed radius and energy called orbits.
II. Electrons revolve only in those orbits where angular momentum of the electron is quantised i.e. $mvr = nh/2\pi$.
III. Energy of an electron in a particular orbit remains constant.
IV. Bohr's frequency rule, $\Delta E = E_2 - E_1 = h\nu$.
Which of the following are incorrect?
(a) All of these *(b)* None of these
(c) I and II *(d)* III and IV

21. The kinetic energy of an electron in the second Bohr's orbit of a hydrogen atom is [a_0 is Bohr radius] **[IIT JEE Main 2012]**
(a) $\frac{h^2}{4\pi^2 ma_0^2}$ *(b)* $\frac{h^2}{16\pi^2 ma_0^2}$ *(c)* $\frac{h^2}{32\pi^2 ma_0^2}$ *(d)* $\frac{h^2}{6\pi^2 ma_0^2}$

22. Find out the number of waves made by a Bohr's electron in one complete revolution in its 3rd orbit. **[IIT JEE Main 1994]**
(a) 1 *(b)* 2 *(c)* 3 *(d)* 4
Hint de-Broglie equation for circumference of Bohr's orbit is given by $2\pi r = n\lambda$.i.e. number of complete waves formed in one complete revolution of electron in any Bohr orbit is equal to the orbit number, hence three.

23. At what minimum atomic number, a transition from $n = 2$ to $n = 1$ energy level would result in the emission of X-ray with $l = 3.0 \times 10^{-8}$ m? **[IIT JEE Main 1993]**
(a) 2 *(b)* 3 *(c)* 4 *(d)* 5

24. Determine the frequency of revolution of an electron in the second Bohr orbit in hydrogen atom.
(a) 5.29×10^{14} Hz *(b)* 8.18×10^{14} Hz
(c) 1.09×10^{14} Hz *(d)* 2.18×10^{14} Hz

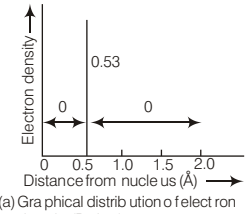
25. If the uncertainties in the measurement of position and momentum of an electron are equal, calculate the uncertainty in measuring the velocity.
(a) 7.98×10^{12} m/s *(b)* 1.16×10^{10} m/s
(c) 1.46×10^{-33} m/s *(d)* 6.95×10^{-7} m/s

QUANTUM MECHANICAL MODEL, ATOMIC ORBITAL, QUANTUM NUMBERS AND ELECTRONIC CONFIGURATION

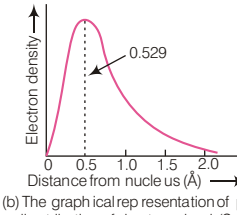
Quantum Mechanical Model of an Atom

This is the most successful model of atom that describes the structure and configuration of atom in three dimensional space.

- This model is based on dual nature of matter and Heisenberg's uncertainty principle.
- Erwin Schrondinger modified Bohr's theory, Bohr considered the position and momentum of electron at a time, i.e. for H-atom, he considered that an electron in ground state always stays at a distance of 0.529Å from the nucleus. While according to Schrodinger, the electron can exists at any distance from the nucleus, but maximum probability is when the distance is 0.529Å from the nucleus.



(a) Graphical distribution of electron density (Bohr's)



(b) The graphical representation of probability distribution of electron cloud (Schrodinger)

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During our approach to wave mechanical model of atom, we will be coming across three key words about the atom which can be defined according to the probability concept as :

1. Orbit It is a two dimensional imaginary space around the nucleus where probability of finding electrons is maximum. It can contain 2 to 32 electrons of variable energy, but same family.
2. Subshell Aggregation or group of orbitals of exactly similar energy which make an orbit. Subshells are named as *s*, *p*, *d* and *f*.
3. Orbital A three dimensional real space around nucleus where probability of finding a particular electron is maximum. An orbital can accommodate maximum of two electrons with exactly equal energy.

He achieved this by considering wave motion of electron in three dimensional space satisfying the following equation

$$\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}+\frac{8\pi^2 m}{h^2}(E-V)\psi=0$$

here, ψ = wave function, h = Planck's constant

E = total energy of electron, i.e. KE + PE

V = potential energy of electron

Different wave functions $\psi, \psi_2, \psi_3 \ldots$ satisfy the above equation having either positive or negative probability of finding electron. As probability can never be negative, ψ^2 is used in place of ψ to represent the probability of finding electron in a small space.

There are three quantum numbers (probability factors) that properly describes the exact position of an electron. Later, one more quantum number called spin quantum number was introduced. These are :

Principal Quantum Number (n)

It describes the principle shell (orbit) in which an electron revolves around the nucleus. Hence, it represents distance of electron from nucleus. It is represented by 'n'.

When $n=1$, the orbit lies closest to nucleus and having minimum energy. The energy of orbit increases as the value of n increases.

K shell < L shell < M shell < N shell (order of energy)

Maximum number of electrons that can be found in an orbit is $2n^2$.

CHEMISTRY CONCENTRATE

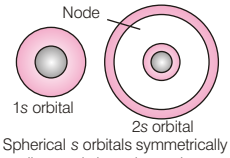
RADIAL AND ANGULAR NODES FOR DIFFERENT ORBITALS

For an s orbital, number of nodes = $(n-1)$ i.e. 1*s* orbital contain no node, 2*s* orbital contains one node, 3*s* orbital contains 2 nodes and so on. Infact nodes are of two types, i.e.

(i) Radial nodes (ii) Angular nodes

A **radial node** is the spherical region around nucleus where probability of finding an electron is zero as shown in the figure of 2*s* orbital.

Similarly, if such a distribution is seen at an angle from the nucleus, the node is called **angular node**.



Spherical *s* orbitals symmetrically disposed about the nucleus

For an orbital, number of nodes are calculated as

Number of radial nodes = $n-l-1$

Number of angular nodes = l, Total nodes = $n-1$

For example, in 3*p* orbitals

Angular node = 1, Radial number = $3-1-1=1$

So, total nodes = 2 (one radial, one angular)

Azimuthal Quantum Number (l)

It describes the name of subshell (*s*, *p*, *d*, *f*) and their shape.

Its value ranges from 0 to $(n-1)$.

n	l	Name of orbital	Shape of orbital	Dependence of probability of finding electron
1	0	*s*	Spherical	Only on distance from nucleus and uniform in all direction.
2	1	*p*	Dumb-bell	Both distance and any one direction (*x*, *y* or *z*).
3	2	*d*	Double bumb-shell	Both distance and any two directions (*xy*, *yz*, *zx*, z^2, or x^2-y^2)
4	3	*f*	Complicated	

Relation between angular momentum and l is given by

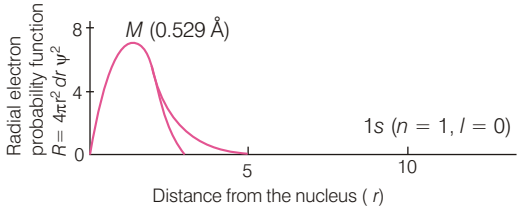
$$mvr=\frac{h}{2\pi}\sqrt{l(l+1)}$$

Magnetic Quantum Number (m)

This describes the splitting of spectral lines under the influence of magnetic field (Zeeman effect).

- When $n=1$, $l=0$ and $m=0$, there exist one spherical *s*-orbital.
- When $n=2$, $l=1$ and $m=-1, 0, +1$. There exists 3 degenerate *p*-orbitals i.e, (p_x, p_y, p_z).
- When $n=3, l=2$ and $m=-2, -1, 0, +1, +2$. There exists five degenerate orbitals as shown below.

If we plot a graph between radial probability function (defined as the probability of finding electron at a distance 'r' from the nucleus), the following results are obtained for different orbitals.



(i) Probability of finding electron at origin (nucleus) is zero.

(ii) The distance for maximum probability of finding electron increases as 'n' increases, e.g. $1s < 2s < 3s$.

(iii) Total number of peaks appearing in the curves for *s*, *p* and *d*-orbitals are equal to n, $(n-1)$ and $(n-2)$ respectively, where 'n' is principal quantum number.

(iv) The curve of 1*s* electron is given below. In the curve, we can interpret the value of R is zero at nucleus, where r is also zero. It then increases as r increases passes through a maximum (peak) at $r=0.529$ Å, which is equal to the radius of Bohr's first orbit and then falls to zero as r tends to infinity. Thus, for 1*s* electron, $R=0$ at $r=0$ and ∞ and R = maximum at $r=0.529$ Å.

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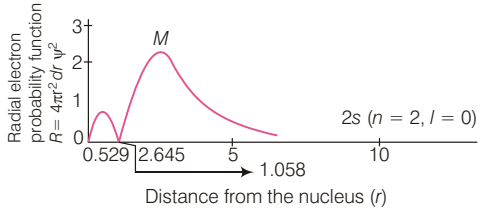
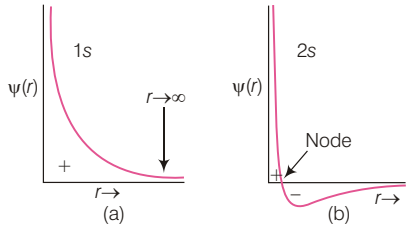
(v) For 2*s* electron, the value of *R* is zero at $r = 0$. The value of *R* increases as *r* increases. Passes through a lower maximum at $r = 0.529$ Å and falls to zero again at $r = 1.058$ Å. *R* reaches second highest at $r = 5 \times 0.529$ Å and then finally approaches zero at *r* tends to infinity. The distance, i.e. 1.058 Å at which the probability of finding electron is zero is called **node** or **nodal plane** or **nodal surface**.



Thus, within the orbital (where probability of finding an electron is maximum), there is space surrounding nucleus where probability of finding electron is zero.

Similar findings are seen in the curves between orbital wave function and *r* with the difference that here negative values of wave function are also visible (because ψ can be negative or positive but ψ^2 can only be positive). For 1s and 2s these curves looks like



- When $n = 4$, $l = 3$ and $m = -3, -2, -1, 0, +1, +2, +3$. There exist seven degenerate orbitals.
- Total number of *m*, for a particular $n = n^2$ Total number of *m*, for a particular $l = (2l + 1)$.
- Each degenerate orbital can hold maximum of two electrons.

Quantum Dots and Their Applications

- A quantum dot (QD) is a crystal of semiconductor material whose diameter is in the order of nanometer range.
- The electronic properties of quantum dots are intermediate between those of bulk semiconductors and of discrete molecules.
- Quantum dots have many applications in transistors, solar cells, LEDs and diode lasers.
- These also acts as agents fo medical imaging.

Spin Quantum Number (*s*)

When electrons in a particular orbit rotate around nucleus, they also rotate (spin) around their own axis, either in clockwise $\left(+\frac{1}{2}\right)$ or in anticlockwise $\left(-\frac{1}{2}\right)$

- Spin angular momentum

$$= \frac{h}{2\pi}\sqrt{s(s+1)}$$

- In diamagnetic species, the magnetic moment (μ) of two opposite spin electrons cancel making net magnetic moment 0.
- In paramagnetic species, all unpaired electrons have same spin and the net magnetic moment equals to $M = \sqrt{n(n+2)}$ BM where, n = number of unpaired electrons.

Pauli's exclusion principle No two electrons can have all the four quantum numbers same. Hence, for two electrons in the same orbital, the *n*, *l* and *m* values are same, but the *s* value is different, i.e. $+\frac{1}{2}$ or $-\frac{1}{2}$ respectively.

Knowledge of quantum numbers is useless if we don't have the knowledge of electronic configuration of elements.

Rules for Filling up of Electrons in Orbitals

(i) **Aufbau principle** Electrons are placed one by one in orbitals in the increasing order of energy level.

The order of increasing energy level can be calculated by $(n + l)$ rule, according to which

1. Lower the value of $n + l$, lower is the energy of the orbital.
2. If $n + l$ value is same for two orbitals, the orbital with lower '*n*' value has lower energy and filled first.

The order in which electrons are filled in the orbitals, according to this rule is

$$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d < 6p < 7s < 5f < 6d < 7p$$

(ii) **Hund's rule** While filling up of electrons in orbitals, pairing of electrons does not take place until each and every degenerate orbital occupies a single electron.

Extra Stability of Completely Filled and Half-filled Orbitals

Elements like Cr, Cu, Nb, Mo, Ru, etc., do not follow Aufbau principle. One electron jumps from lower energetic 4*s* orbital to higher energetic 3*d* in Cr and Cu to obtain half-filled and fully filled configuration respectively.

Electronic configuration of such elements are given below :

- Cr-24 – $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^5, 4s^1$
- Cu-29 – $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}, 4s^1$
- Nb-41 – [Kr] $4d^4, 5s^1$
- Mo-42 – [Kr] $4d^5, 5s^1$
- Ru-44 – [Kr] $4d^7, 5s^1$
- Rh-45 – [Kr] $4d^8, 5s^1$
- Pd-46 – [Kr] $4d^{10}, 5s^0$
- Ag-47 – [Kr] $4d^{10}, 5s^1$
- Pt-78 – [Xe] $4f^{14}, 5d^9, 6s^1$
- Au-79 – [Xe] $4f^{14}, 5d^{10}, 6s^1$
- La-57 – [Xe], $4f^0, 5d^1, 6s^2$
- Ac–89–[Rn], $5f^0, 6d^1, 7s^2$

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Best Practice SHOTS

26. Which of the following statements are true about the wave function?

I. When an electron is in an energy state, the wave functions corresponds to that energy state and contain all information about the electron.

II. It is a mathematical function whose value depends upon the coordinates of the electron in the atom and does not carry any physical meaning.

III. Wave functions of hydrogen or hydrogen like species with one electron are called atomic orbitals.

IV. Wave functions pertaining to one-electron species are called one-electron system.

The correct set of statements is

(a) I, II and III *(b)* III and IV *(c)* I and II *(d)* All of these

27. What is true about probability density?

I. Probability density is denoted by $|\Psi|^2$.

II. It is the probability of finding an electron at a point within an atom is proportional to the square of the orbital wave function.

III. From the value of $|\Psi|^2$ at different points, within an atom, it is possible to predict the region around the nucleus where electron will most probably be found.

Choose the correct option.

(a) I and II *(b)* II and III *(c)* I and III *(d)* All of these

28. Match the following quantum number (Column I) with the information provided by (Column II) Select the correct codes from the given options.

Column I (Quantum number)	Column II (Information provided)
A. Principal quantum number	p. Orientation of the orbital
B. Azimuthal quantum number	q. Energy and size of the orbital
C. Magnetic quantum number	r. Spin of electron
D. Spin quantum number	s. Shape of the orbital

Codes

	A	B	C	D
(a)	q	s	p	r
(c)	p	q	r	s

	A	B	C	D
(b)	r	s	q	p
(d)	s	r	q	p

29. Consider the following statements,

I. The attractive interaction of an electron increases with increase of positive change (Z_e) on the nucleus.

II. Due to the presence of electrons in the inner shells, the electrons in the outer shell will not experience the full positive charge of the nucleus (Z_e).

III. The effect will be lowered due to the partial screening of positive charge on the nucleus by inner shell electrons. This is known as the shielding of the outer shell electrons from the nucleus by the inner shell electrons.

IV. The net positive charge experienced by the other electrons is known as effective nuclear charge (Z_{eff})

The correct statements are

(a) I, II and III *(b)* II, III and IV
(c) I, II and IV *(d)* All of these

30. Consider the following statements,

I. For an atom having a single electron, the principal quantum number (n) is only a parameter to determine the energy of the orbital.

II. In case of multielectron atoms, the energy of an electron depends not only on its principal quantum number but also on its azimuthal quantum numbers, $(n + l)$ rule is followed.

III. The energies of the orbitals in the same sub-shell decrease with an increase in the atomic number, i.e. $E_{25(H)} > E_{25(Li)} > E_{25(Na)} > E_{25(K)}$

IV. Z_{eff} experienced by the orbital decreases with an increase in the azimuthal quantum number and thus order of energies of various sub-shells within an energy level is $s < p < d > f \ldots$.

V. Z_{eff} decreases with an increase in the value of principal quantum number (n) $\therefore 4s < 3s < 2s < 1s$.

The correct set of statements is/are

(a) I, II and III *(b)* IV and V
(c) II, III and IV *(d)* All of these

31. The stability of an electron in multi-electron atom is because

(a) total attractive interactions >total repulsive interactions
(b) total attractive interactions = total repulsive interactions
(c) total attractive interactions < total repulsive interactions
(d) it is independent of interactions amongst electrons

32. The quantum numbers of electrons are given below.

Case	n	l	m_l	m_s
I.	4	2	− 2	$-\frac{1}{2}$
II.	4	1	0	$+\frac{1}{2}$
III.	3	2	− 2	$-\frac{1}{2}$
IV.	4	1	+ 1	$+\frac{1}{2}$

The correct order of increasing energies are

(a) IV >III = II >I *(b)* IV < III = II < I
(c) IV < III < II < I *(d)* IV < II < III < I

33. Which combination of quantum numbers n, l, m and s for the electron in an atom does not provide a permissible solution to the wave equation?

(a) 3, 2 −2, $+\frac{1}{2}$ *(b)* 3, 3, 1, $-\frac{1}{2}$
(c) 3, 2, 1, $+\frac{1}{2}$ *(d)* 3, 1, 1, $-\frac{1}{2}$

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34. Suppose that Pauli exclusion principle states that an orbital can accommodate three electrons, what are the respective atomic numbers of the second members of alkali metal family and the first member of halogen family?
(a) 16, 14 (b) 11, 9
(c) 16, 9 (d) 34, 17

35. Which of the following should be correct according to Hund's rule?

(a) $_6C = 1s^2\,2s^2$ 2p: ⇅ | | | (b) $_8O = 1s^2\,2s^2$ 2p: ⇅ | ⇅ | |
(c) $_7N = 1s^2\,2s^2$ 2p: ⇅ | 1 | | (d) $_9F = 1s^2\,2s^2$ 2p: ⇅ | ⇅ | 1

36. The orbital diagram in which Aufbau principle is violated?

(a) ⇅ | ⇅ | 1 | (b) 1 | ⇅ | 1 | 1
(c) ⇅ | 1 | 1 | 1 (d) ⇅ | ⇅ | ⇅ | 1

37. For a *d*-electron, the orbital angular momentum is
(a) $\sqrt{6}\left(\frac{h}{2\pi}\right)$ (b) $\sqrt{2}\left(\frac{h}{2\pi}\right)$ (c) $\left(\frac{h}{2\pi}\right)$ (d) $2\left(\frac{h}{2\pi}\right)$

38. The electronic configuration of an element is $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^5, 4s^1$. This represents its
(a) excited state (b) ground state
(c) cationic form (d) anionic form

39. Among the following series of transition metal ions, the one in which all metal ions have $3d^2$ electronic configuration is
(At. no. of Ti = 22, V = 23, Cr = 24 and Mn = 25)
(a) $Ti^{3+}, V^{2+}, Cr^{3+}, Mn^{4+}$ (b) $Ti^{+}, V^{4+}, Cr^{6+}, Mn^{2+}$
(c) $Ti^{4+}, V^{3+}, Cr^{2+}, Mn^{3+}$ (d) $Ti^{2+}, V^{3+}, Cr^{4+}, Mn^{5+}$

40. The quantum numbers of the last electron of an element are given below. Predict the atomic number and name of the element from the following quantum numbers. $n = 3, l = 2, m = 0, s = -\frac{1}{2}$
(a) V (b) Sc (c) Cu (d) Ni

Answers

1. (d)	**2.** (a)	**3.** (d)	**4.** (b)	**5.** (d)	**6.** (c)	**7.** (c)	**8.** (b)	**9.** (a)	**10.** (a)
11. (b)	**12.** (b)	**13.** (a)	**14.** (b)	**15.** (d)	**16.** (c)	**17.** (c)	**18.** (c)	**19.** (d)	**20.** (b)
21. (c)	**22.** (c)	**23.** (a)	**24.** (b)	**25.** (a)	**26.** (d)	**27.** (d)	**28.** (a)	**29.** (d)	**30.** (d)
31. (a)	**32.** (b)	**33.** (b)	**34.** (a)	**35.** (d)	**36.** (b)	**37.** (a)	**38.** (b)	**39.** (d)	**40.** (a)

MASTER STROKES

1. Which of the following statements is true regarding absorption and emission spectra?
(a) Emission spectrum is observed, when white light is passed through the substance and the transmitted radiations are analysed by the spectroscope
(b) Absorption spectra is always discontinuous whereas emission spectra may be continuous or may be discontinuous
(c) Absorption spectrum gives bright lines (coloured) on dark background whereas emission spectrum gives dark lines on bright background
(d) Radiations from emitting source are analysed by the spectroscope in absorption spectrum

2. Calculate the energy of α-particle approaching the nucleus of copper atom upto 10^{-13} m distance form the nucleus of an atom?
(a) 1.33×10^{-13} (b) 6.34×10^{-16} (c) 1.33×10^{-16} (d) 6.34×10^{-13}
Hint At the nuclear border of atom α-particle stops.

$$KE = PE = \frac{K \times q_1 q_2}{r}$$

where, q_1 = charge on nucleus, q_2 = charge on α-particle, $K = 9 \times 10^9$, $e = 1.6 \times 10^{-19} C$, Cu (at. no. = 29), $r = 10^{-13}$ m.

3. According to Bohr's Theory, E_n = Total energy; K_n = kinetic energy V_n = potential energy; r_n = Radius of *n*th orbit. **[IIT JEE Main 2006]**

Match the following.

Column I	Column II
A. $V_n / K_n = ?$	p. 0
B. $r_n \mu E_n^x, x = ?$	q. –1
C. Angular momentum in lowest orbital	r. –2
D. $\frac{1}{r_n} \mu Z^y, y = ?$	s. + 1

Codes

	A	B	C	D		A	B	C	D
(a)	p	q	r	s	(b)	r	p	q	s
(c)	s	r	q	p	(d)	q	s	p	r

4. An electron beam of 1.54 Å wavelength is accelerated so that it can undergo diffraction by crystals. Calculate the potential required for acceleration.
(a) 63.3 V (b) 16.02 V
(c) 91.08 eV (d) 39.08 eV
Hint $\frac{1}{2} mv^2 = eV$ and $\lambda = \frac{h}{mv}$

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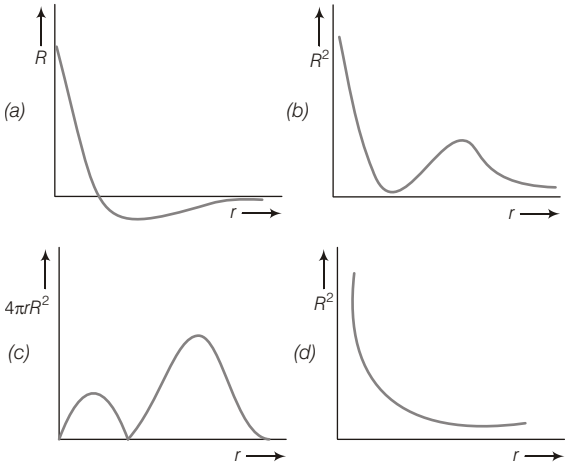
5. A compound of vanadium has a magnetic moment of 1.73 BM. The electronic configuration of vanadium is

(a) $[Ar]\,3d^3\,4s^0$ (b) $[Ar]\,3d^1\,4s^2$
(c) $[Ar]\,3d^1\,4s^2$ (d) $[Ar]\,3d^1\,4s^0$

6. Variations of radial wave function R against distance r is given for 2*s*-orbital. Select the incorrect one.

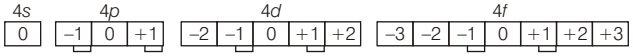


Hint Graph is for 1*s*-orbital with no node. (a), (b) and (c) are for 2*s*-orbital (with one node). R^2 = Radial probability density ; $4\pi r^2R^2$ = radial distribution function.

7. In an atom, the total number of electrons having quantum numbers $n = 4$, $|m_l| = 1$ and $m_s = -\frac{1}{2}$ is

(a) 4 (b) 5 (c) 6 (d) 7

Hint For $n = 4$, possible orbitals are



Number of orbitals having $|m_l| = 1$ are 6.
Number of electrons having
$m_s = -\frac{1}{2}$ in these orbitals are one each. ∴ 6 electrons

8. The wave function of 2*s* electron is given by

$$\psi_{2s} = \frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left(2 - \frac{r}{a_0}\right)e^{-r/a_0}$$

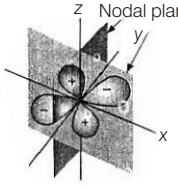
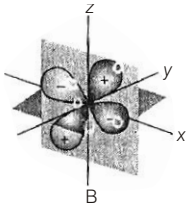
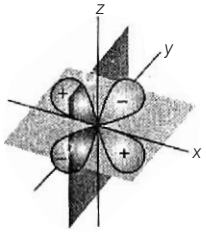
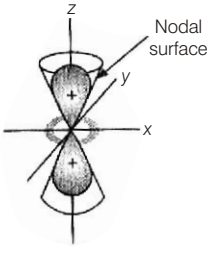
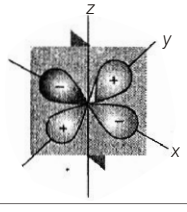
It has a node at $r = r_0$, find the relation between r_0 & a_0.

(a) $r_0 = 2a_0$ (b) $r_0 = 3.9a_0$ (c) $r_0 = 2a_0$ (d) $r_0 = 2.8a_0$

9. In Heisenberg's uncertainty experiment, which of the statements is incorrect?

(a) Use of high intensity light increases accuracy in the measurement of distance of electron from nucleus
(b) Use of high frequency light increases accuracy in the measurement of distance of electron from the nucleus
(c) Use of long wavelength light increases accuracy in the measurement of speed of electron
(d) If an experiment is designed to measure the distance of electron from nucleus, the speed measured in same experiment would be highly imprecise

10. Match the (Column I) with (Column II) and choose the correct option from the codes given below.

Column I (Boundary surface diagram)		Column II (*d*-orbital)	
A.		p.	d_{z^2}
B.		q.	$d_{x^2-y^2}$
C.		r.	d_{yz}
D.		s.	d_{xz}
E.		t.	d_{xy}

Codes

	A	B	C	D	E		A	B	C	D	E
(a)	s	t	q	p	r	(b)	t	r	s	p	q
(c)	r	s	t	q	p	(d)	t	s	p	q	r

Answers

1. (b) **2.** (a) **3.** (b) **4.** (a) **5.** (d) **6.** (d) **7.** (c) **8.** (a) **9.** (a) **10.** (b)

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Chemical Bonding

INTRODUCTION, IONIC BOND AND COVALENT BOND

Chemical Bond

It is either interatomic, intermolecular or interionic attraction which holds the constituent species together to form a more stable compound. Naturewise any type of bond contains ELECTROSTATIC FORCES OF ATTRACTION only.

- Bonds are of the following types:
  (a) Ionic bond
  (b) Covalent bond
  (c) Coordinate bond
  (d) Metallic bond
  (e) Hydrogen bond
  (f) van der Waals' forces of attraction
- The main reason behind a chemical bond formation is to attain nearest stable inert gas configuration.

Kossel-Lewis Approach to Chemical Bond Formation (Octet Rule)

This concept was proposed by **Kossel** and **Lewis**, called **electronic concept of valency** or **octet rule. Langmuir** later on extended it.

The main points of this concept are as

(i) The outermost shell of an atom is called the **valence shell** and the electrons present in it are called **valence electrons**.

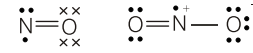
(ii) Inert gases are stable due to their stable electronic configuration or due to the presence of eight electrons in their valence shell.

(iii) Elements that do not have complete octet have a high tendency to attain this configuration either by losing or gaining or sharing electron to or with the atoms of same or other elements. In other words, bonds are formed between the atoms, to attain stability. Depending upon the way of combining, the bonds may be ionic (formed by losing and gaining of electrons) or covalent (formed by sharing of electrons).

Violation of Octet Rule

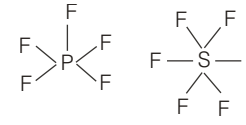
The octet rule is violated in a significant number of cases. These are :

1. Be and B have less than four valence electrons, hence their octet cannot be completed even if they bind to their full strength.
2. In molecules with an odd number of electrons, the octet rule is not satisfied by all the atoms, e.g. in molecules like NO and NO_2.

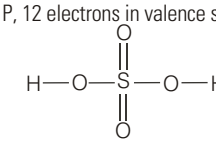


Total 7 electrons in nitrogen atom

3. In a number of compounds there are more than 8 valence electrons present in the central atom. This is termed as expanded octet. This tendency is seen in elements beyond the 3rd period of periodic table as they have vacant *d*-orbitals for bonding, e.g. PF_5, SF_6, H_2SO_4 etc.



10 electrons in valence shell of P, 12 electrons in valence shell of S.



12 electrons in valence shell of S

The other drawbacks of octet rule include

1. The shape of the molecule is not clear.
2. It is totally silent about the energy of the molecule, i.e. relative stability.

Electrovalent (or Ionic) Bond

The bond formed due to complete transfer of electrons from the electropositive atom to the electronegative atom is called electrovalent bond.

- The number of electrons lost or gained by an atom during the formation of electrovalent bond is called electrovalency of that atom.

Transference of electron is not the necessary condition for this type of bonding, rather it is considered as generalised condition. Such attractive forces can be seen between any two oppositely charged atoms or ions even from different sources.

Factors Affecting Formationof Ionic Bond

Easier the formation of ions, easier is the formation of ionic bond thus, it depends on the following factors :

(i) Low ionisation enthalpy of the electropositive elements.

(ii) High negative value of electron gain enthalpy of the electronegative elements.

(iii) Lattice enthalpy of the ionic compounds should be high.

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Variable Valency

A number of elements like Cu, Au, Hg, Sn, Pb, Fe, Co, Ni, Sb, Sc etc., show more than one valency in their compounds. The reasons for such a variable valency (i.e. electrovalency) are :

1. Instability of core in case of most of the transition elements, e.g. Cu shows electrovalencies 1 and 2 as :
   Cu (29) – $[Ar]3d^{10}, 4s^1$
   However, Cu^+ – $[Ar]3d^{10}$ less stable
   Cu^{2+} – $[Ar]3d^9$ more stable (in solution)
   The $s^2p^6d^{10}$ configuration of Cu^+ is not as stable as $s^2p^6d^9$ configuration in solution. The nuclear charge is not strong enough to hold all the electrons intact in case of Cu^+, thus Cu^{2+} ion is more stable.
2. Inert pair effect (i.e. tendency of *s*-electrons to remain together or reluctance of *s*-electrons to participate in a reaction) in *p*-block elements.

Characteristics of Ionic Compounds

(i) These are crystalline solids at normal temperature and pressure with high melting and boiling points, stability and density.

(ii) These are very hard and brittle, as the crystalline planes can be separated easily.

(iii) These are, in general, highly soluble in polar solvents like water, because the high value of solvation or hydration enthalpy which is sufficient to break the lattice structure.

(iv) Ionic compounds do not conduct electricity in solid state, but are good conductor of electricity, either in fused state or when dissolved in a solvent of high dielectric constant due to ionic mobility .

(v) Ionic compounds undergo very fast reactions in solution which are mainly ion exchange reactions.

(vi) Ionic compounds with same electronic configuration are usually isomorphous (having same lattice structure).

(vii) Ionic bonds are non-directional and do not exhibit isomerism in space.

REMEMBER

For the dissociation of an ionic compound in solvent, solvation energy should be greater than lattice energy. Dissociation is also favoured by high dielectric constant of solvent.

Solvent	H_2O	CH_3OH	C_2H_5OH	CH_3COCH_3	CH_3OCH_3
Dielectric constant	81	35	27	21	4.1

(Capacity to dissolve ions decreases)

Lattice Enthalpy (*U*)

The amount of energy evolved when gaseous positive and negative ions combine to form one mole of soild ionic compound is called lattice enthalpy.

- Lattice enthalpy μ charge of ions $\mu \frac{1}{\text{size of ions}}$
- Lattice enthalpy depends on various factors like ionisation enthalpy, electron gain enthalpy, heat of sublimation, dissociation energy etc. Hence, its value is indirectly calculated from Born-Haber cycle by applying Hess law.

Born-Haber Cycle

According to this, the formation of an ionic crystal may occur either by the direct combination of the elements or by an alternate process in which

(i) the reactants are vaporised to convert in gaseous state.

(ii) the gaseous atoms are converted into ions.

(iii) the gaseous ions are combined to form ionic lattice of molecules. e.g. $M(s) + \frac{1}{2}X_2(g) \rightarrow MX(s);\ \Delta H_1 = Q$

Alternatively,

(i) $M(s) \rightarrow M(g);$ $\Delta H = S$

(ii) $M(g) \rightarrow M^+(g) + e^-;$ $\Delta H = I$

(iii) $\frac{1}{2}X_2(g) \rightarrow X(g);$ $\Delta H = \frac{D}{2}$

(iv) $X(g) + e^- \rightarrow X^-(g);$ $\Delta H = -E$

(v) $M^+(g) + X^-(g) \rightarrow MX(s);$ $\Delta H = -U$

$$\Delta H_2 = S + I + \frac{D}{2} - E - U$$

where, S = enthalpy of sublimation
I = ionisation enthalpy
D = dissociation enthalpy
E = electron gain enthalpy

ΔH_1 and ΔH_2 represent the enthalpy change of same chemical change. Hence, $\Delta H_1 = \Delta H_2$

$$\therefore \quad Q = S + I + \frac{D}{2} - E - U$$

$$\therefore \quad U = S + I + \frac{D}{2} - E - Q$$

LATTICE ENTHALPY AND SOLUBILITY

Lattice enthalpy plays an important role in deciding the solubility of ionic solids. It affects the solubility in the following manner :

1. If anion and cation are of comparable size, the cationic radius will influence the lattice energy. Since, lattice energy decreases much more than the hydration energy with increasing ionic size, solubility will increase as we go down the group.
2. If the anion is large compared to the cation, the lattice energy will remain almost constant within a particular group. Since, the hydration energies decrease down a group, solubility will decrease as found for alkaline earth metal carbonates and sulphates.

The energy transactions associated with this process comes under the category of Born-Haber cycle. The simplest example of such a cycle is given above.

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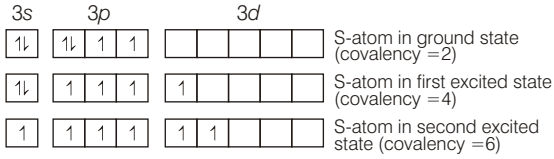
Covalent Bond

When two atoms of comparable electronegativity value share electron pair with each other, the bond formed is called covalent bond.

- The number of electrons contributed by an atom while sharing with other atom(s) to achieve inert gas configuration is called covalency.
- Generally, the covalency of an element is equal to the total number of unpaired electrons present in *s* and *p*-orbitals. The elements having vacant *d*-orbitals in their valence shell (e.g. P, S, Cl, As, Sn, etc.) show variable covalency by increasing the number of unpaired electrons during excited conditions. The maximum covalency of the elements in different period is:
  (i) 4 for the elements of second period.
  (ii) 6 for the elements of 3rd and 4th period.
  (iii) 8 for the elements of 5th period onwards.
- Such a variation in maximum covalency can be explained on the basis of absence of vacant *d*-orbitals in 2nd period elements and their availability in 3rd period and subsequent elements, e.g. sulphur.



CHEMISTRY CONCENTRATE
NUMBER OF COVALENT BONDS

The number of covalent bonds are calculated as :

Number of covalent bonds between two atoms $= \frac{\text{electron shared}}{2}$.

The following mathematical relationship can be used to determine the total number of electrons shared $S = N - A$.

Here, S = total number of electrons shared in the molecule or polyatomic ion.

N = the number of valence shell electrons needed by all the atoms in the molecule or ion to achieve noble gas configuration.

[$N = 8 \times$ number of atoms (H excluded) $+ 2 \times$ number of H-atoms].

A = the number of electrons available in the valence shell of all of the representative atoms. This is equal to the sum of their periodic group number.

Lewis Structure Representation of Covalent Molecules

Lewis structure of a molecule gives us an idea about the number of electron pairs shared between atoms in a molecule.

Formal Charge

In a polyatomic ion, the net charge possessed by the species is not due to a particular atom, rather it is due to different atoms, which is called formal charge of an atom.

Formal charge (FC) of an atom is calculated as: $FC = V - \left[lp + \frac{1}{2} bp \right]$

where, V = total number of valence electrons in the free atom.

lp = total number of non-bonding electrons or lone pairs.

bp = total number of bonding electrons or bond pairs.

Covalent Bonding and Fajans' Rule

- Covalent bonding is favoured by those factors that favour polarisation. Polarisation is the increase in the covalent character of an ionic bond due to the attraction between loosely bonded valence electrons of larger anions by the smaller cations.

The following rules are followed for deciding polarisation and hence covalent character:

(a) **The charge on cation or anion must be larger** The increased charge increases the polarisation of other ion (anion), thus, covalent character is increased.

(b) **The cation must be smaller** Because smaller size increases the positive charge density of cation, causing more polarisation of anion.

(c) **The anion must be larger** Because, the outer electrons will be at a greater distance from the nucleus, hence, more easily influenced by the attractive forces of cation. As a result, larger anions will be more easily polarised in comparison to smaller anions.

(d) The polarising power of those cations which do not have inert gas configuration will be more in comparison to cations having inert gas configuration, e.g. polarising power of Cu^+ ion is more in comparison to the polarising power of Na^+ ion.

Covalent Bond Characters

Bond Length The average distance between the centre of nuclei of two bonded atoms in a molecule is called bond length. It depends on size of atom, hybridisation, steric effect and resonance effect.

Bond Enthalpy It is the amount of energy required to break all the bonds in one mole of gaseous molecule.

Bond enthalpy μ electronegativity difference

$$\mu \frac{1}{\text{size of atoms}}, \quad \mu \frac{1}{\text{number of lone pairs}}$$

Bond Order It is the number of covalent bonds present between two atoms in a molecule. Bond order μ bond enthalpy $\mu \frac{1}{\text{bond length}}$. Hence, higher the bond length, lower is the bond order and bond dissociation enthalpy.

Bond Angles It is the angle between the bonded orbitals. Bond angle $\mu \frac{1}{\text{number of lone pairs}}$

Bond angle decreases, when the electronegativity of central atom decreases. However, among molecules with same central atom bond angle increases as the electronegativity of surrounding atoms decreases.

e.g. $\underset{104.5^\circ}{H_2O} > \underset{92^\circ}{H_2S} > \underset{91^\circ}{H_2Se} > \underset{89^\circ}{H_2Te}$, $\underset{102^\circ}{PI_3} > \underset{101.5^\circ}{PBr_3} > \underset{100^\circ}{PCl_3}$

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Characteristics of Covalent Compounds

These are gases or liquids at standard temperature and pressure. Some molecules with higher molecular weight also exist as soft solids.

(i) They have low melting and boiling points, with the exception of diamond, silicon carbide, silica, etc.

(ii) Covalent compounds, either in fused or in solid state are bad conductor of electricity, with an exception of graphite, which conduct electricity due to the presence of free electrons.

(iii) Covalent compounds, in general are insoluble in polar solvents like water, but soluble in non-polar solvents like benzene, CCl_4. However compounds making hydrogen bond with water are soluble in water.

(iv) Reactions involving covalent compounds are slow, as it involve the fission of older bonds and formation of new bonds.

Polar and Non-polar Covalent Bonds

Polar covalent bond When the covalent bond is formed between two heteronuclear atoms (different electro-negativity), the bond formed has partial ionic character, as the electron pair is attracted by the more electronegative atom. Such a bond is called polar covalent bond. In this case the net dipole moment does not cancel each other

e.g. $\overset{\delta+}{H}\text{----}\overset{\delta-}{O}\overset{\delta-}{}\text{----}\overset{\delta+}{H}$, $\overset{\delta+}{H}\text{----}\overset{\delta-}{Cl}$

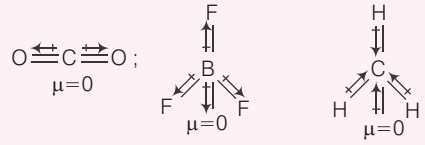
Non-polar covalent bond When the covalent bond is formed between two homonuclear atoms (atoms of equal electronegativity), the electron pair is equally shared between them cancelling the net dipole moment to zero. Such a bond is called non-polar covalent. e.g. Cl_2, F_2, CCl_4, CH_4, etc. Bond polarity affects both physical and chemical properties. Physical properties affected are melting and boiling points and solubility, etc.

Dipole Moment (μ)

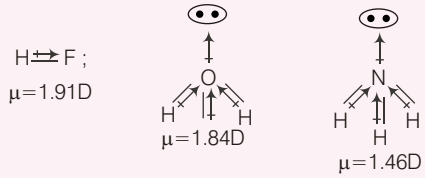
It is defined as the product of net charge and distance between the two charges (bond length). μ = charge × bond length.

- **Units** In CGS – debye (D), SI – coulomb × metre
- Dipole moment is a vector quantity represented by the symbol, $\mapsto$, where the arrow mark is pointed towards negative end.

For symmetrical molecules as given below, dipole moment is zero.



However, unsymmetrical molecules have some dipole moment as:



Formulae for Percentage Ionic Character

The ionic character in a polar bond can be calculated by the following methods:

1. Pauling gave the following equation to calculate the percentage ionic character of a polar bond by using electronegativity difference $(x_A - x_B)$: Amount of ionic character in

   $A-B$ bond $= [1 - e^{0.25(x_A - x_B)}]\%$ or $[18(x_A - x_B)^{1.4}]\%$

   With the help of this equation, Pauling established the following relation:

$(x_A - x_B)$	–	0.6	1.0	1.4	1.7	2.0	2.4	3.0	3.2
% ionic character	–	9	22	39	51	53	76	91	92

2. Hannary and Smith also used the electronegativity difference $(x_A - x_B)$ to find the percentage ionic character by the following expression:

   Ionic character in $A-B$ bond $= [16(x_A - x_B) + 3.5(x_A - x_B)^2]\%$

3. By using dipole moment, percentage ionic character of a polar bond $(A-B)$ is calculated as: Percentage ionic character

   $$= \frac{\mu_{exp}}{\mu_{cal}} \times 100 = \frac{\mu_{exp}}{d_{A-B} \times e} \times 100$$

   here, μ_{exp} = experimental (or observed) value of dipole moment of AB molecule, μ_{cal} = calculated (theoretical) value of dipole moment of AB molecule when the molecule was assumed to be completely ionic. This value can be calculated as, $d \times e$, i.e. bond length × charge.

Best Practice SHOTS

1. Which of the following statements is incorrect about chemical bonding?

(a) Potential energy of atoms decreases during bond formation

(b) Bonded atoms are more stable than unbonded atom due to their higher potential energy

(c) Normally only electron in outermost shell of an atom are involved in bond forming

(d) When two atoms approach each other, repulsive as well as attractive forces both act between them

2. When ammonia donate its lone pair to boron trifluoride, an adduct is formed. The geometry of adduct will be

(a) square planar (b) tetrahedral

(c) trigonal bipyramidal (d) octahedral

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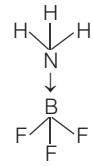
Hint $\ddot{N}H_3 + BF_3 \longrightarrow$ 

3. Choose the correct option.

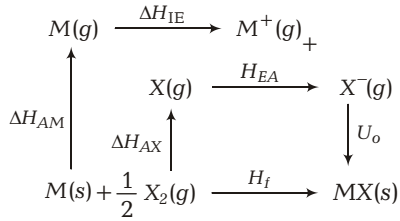
(a) Covalent compounds are able to conduct electricity in liquid state
(b) In ionic compounds, the attraction between ions is electrostatic and is non-directional, extending equally in all direction
(c) Ionic compounds are usually soluble in polar solvents having low dielectric constant
(d) All of the above

4. Select the correct order for melting point.

(a) CuCl < LiCl < NaCl < KCl
(b) LiCl < NaCl < KCl < CuCl
(c) LiCl < CuCl < KCl < NaCl
(d) KCl < CuCl < NaCl < LiCl

Hint Cation having 18 electrons in their outer shell have more covalent character.

5. The Born-Haber cycle,



[ΔH_{AM} and ΔH_{AX} are the enthalpies of atomisation of the metal and the non-metal]

Which of the following is the correct option?

(a) $\Delta H_f = \Delta H_{AM} + \Delta H_{AX} + \Delta H_{IE} + \Delta H_{EA}$
(b) $U_O = \Delta H_f + \Delta H_{EA} + \Delta H_{AM} + \Delta H_{AX}$
(c) $\Delta H_f = \Delta H_{AM} + \Delta H_{AX} + \Delta H_{IE} + \Delta H_{EA} + U_O$
(d) $\Delta H_{IE} = \Delta H_f + \Delta H_{EA} + U_O$

6. A number of ionic compounds, e.g. AgCl, CaF_2, $BaSO_4$ are insoluble in water. This is because

(a) these molecules have exceptionally high attractive forces in their lattice
(b) water is not a good ionising solvent
(c) water has a high dielectric constant
(d) ionic compounds do not dissolve in water

7. Maximum covalence of an atom of an element is equal to

(a) total number of electrons in the *p*-orbitals of valence shell
(b) total number of electrons in the *s*-and *p*-orbitals of valence shell
(c) number of unpaired electrons in the *p*-orbitals of valence shell
(d) number of unpaired electrons in the *s*-orbitals and *p*-orbitals of valence shell

8. Select the correct statement.

(a) When a covalent bond is formed, transfer of electrons take place
(b) Pure H_2O does not contain any ion
(c) A bond is formed when attractive forces overcome repulsive forces
(d) HF is less polar than HBr

9. Which of the respective order is correct?

(a) $BeCO_3 > SrCO_3 > BaCO_3$: K_p value order during their thermal dissociation in close container
(b) $NH_3 > SbH_3 > AsH_3 > PH_3$: Thermal stability order
(c) Liq. hydrogen < liq. helium : Boiling point order
(d) $O_2 < KO_2 < K_2O_2$: Bond order

Hint According to Fajan rule, ionic potential of cation increases thermal stability decreases hence K_p increases because reaction move in forward direction.

10. Which of the following is not correct?

(a) Difference in electronegativities of combining atoms can lead to dipole moment
(b) CO_2 molecule has dipole moment
(c) Dipole moment is vector quantity
(d) Lone pair of electrons present of central atom can give rise to dipole moment

11. Which one of the following pairs of molecules will have permanent dipole moments for both members?

(a) SiF_4 and NO_3
(b) NO_2 and CO_2
(c) NO_2 and O_3
(d) SiF_4 and CO_2

12. What type of a non-covalent bond would be expected, if there is an *M*—H moiety and a group *X*—H with positive hydrogen atom?

(a) H—*M*—*X*—H *(b)* H—*M*—H—*X*
(c) *M*—H—H—*X* *(d)* *M*—H—*X*—H

Hint Non-covalent bond refer to dipole-dipole interaction.

13. Na^+ and F^- are isoelectronic, yet their ionic radii are different. The reason is

(a) Sodium is a metal and fluorine is a non-metal
(b) Na^+ is more reactive than F^-
(c) Sodium is electropositive and fluorine is electronegative
(d) Effective nuclear charge for the 2*p* electrons in F^- is much smaller than it is in Na^+

14. Among N_2, N_3^-, azobenzene and hydrazine, the shortest and longest N—N bond distances are found, respectively in

(a) N_2 and azobenzene *(b)* N_3^- and azobenzene
(c) N_2 and hydrazine *(d)* N_3^- and hydrazine

15. For BF_3 molecule which is incorrect?

(a) It has weak B—F bonds
(b) It has low Lewis acidity than BCl_3
(c) It has a plane of symmetry
(d) It has a bond order of 1.33

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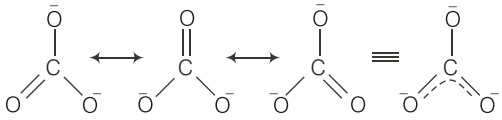
RESONANCE, VBT, HYBRIDISATION AND VSEPR THEORY

Resonance

The phenomena in which two or more structures can be written for a molecule or ion but none of them could represent the structure completely is known as resonance and such type of structures are called resonance structures or canonical forms.

- The actual molecule is considered to have a structure equivalent to average of all these canonical forms.



- From the concept of resonance, the bond order (BO) of a molecule (or ion) is calculated as,

$$BO = \frac{\text{Total number of bonds between two atoms in all the structures}}{\text{Total number of canonical forms}}$$

- The stability of a resonance structure can be decided by considering the following points :
  1. A non-polar canonical form is more stable.
  2. More the number of covalent bonds, more is the stability.
  3. Resonance structure in which negative charge resides on more electronegative atom and positive charge on less electronegative atom is more stable as compared to that for which opposite is true.

MISCONCEPTIONS IN RESONANCE

Many misconceptions are associated with resonance. You should remember that :

The canonical forms have no real existence.

The molecule does not exist for a certain fraction of time in one canonical form and for other fractions of time in other canonical forms.

There is no such equilibrium between the canonical forms as we have between tautomeric forms (keto and enol) in tautomerism.

The molecule as such has a single structure which is the resonance hybrid of the canonical forms and which cannot be depicted by a single Lewis structure.

Valence Bond Theory (VBT)

This theory proposed by **Heitler** and **London** having the following postulates:

A covalent bond is formed, when the orbital of one atom containing unpaired electron overlaps with the orbital of another atom containing unpaired electron. This results in the formation of hybrid orbitals which is occupied by both electrons.

The two electrons occupying the hybrid orbital must have opposite spin.

The electron pairs are shared by both the nuclei and electron density is maximum in between the two atoms.

The strength of a chemical bond is proportional to the extent of overlapping of two atomic orbitals.

Overlapping of only those atomic orbitals occur, whose electrons take part in the bond formation.

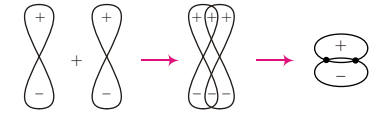
Between two orbitals of same stability, the one with more directionally concentrated cloud would form a stronger bond, e.g. *p*-orbital forms a stronger bond than *s*-orbital.

s-orbital, being spherical does not show any preference in direction. But *p*-, *d*-, and *f*-orbital tend to form a bond in their direction of maximum electron density.

OVERLAPPING OF ORBITALS

These are of the following types :

1. End to end or axial or head on overlapping This results in the formation of σ-bond. In such overlapping, the electron density is concentrated in between the two atoms.
2. Sidewise overlapping or parallel overlapping This results in the formation of π-bond. This occurs after at least one head on overlapping of atomic orbitals. Here also the electron density is concentrated between the atoms, but on either side of line joining the nuclei as shown below:



p_X atomic orbital | p_X atomic orbital | Overlapping of p_X atomic orbitals by the linear additive combination | Resultant $\pi(2p_X)$ BMO

A single bond (—) contains 1 σ-bond and no π-bond, double bond (═) contains 1 σ and 1 π-bond and a triple bond (≡) contains 1 σ and 2π-bonds.

Hybridisation

Combining the wave functions of atomic orbitals of nearly equal energy containing unpaired electron to form new hybrid orbitals of nearly equal energy is called hybridisation.

- The atomic orbitals involved in π-bond formation do not participate in hybridisation due to sidewise overlapping.
- In some cases empty orbitals also participate in hybridisation. Atomic orbitals having lone pair of electrons also participate in hybridisation.
- The electronic charge in hybrid orbitals is concentrated more in one direction, which favours the overlapping of hybrid orbitals. This results in the formation of a larger and a smaller lobe.
- The hybrid orbitals have equivalent energy and identical shape and size. Hence, hybrid orbitals are degenerate.
- The shape of hybrid orbitals are different from that of participating atomic orbitals.

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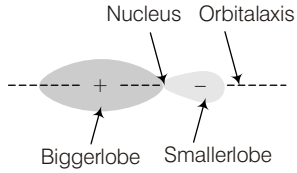
{JEE FINAL TOUCH}



Representationofahybridorbital

An alternative way of finding hybridisation is the use of following formula: $H = \frac{1}{2}[V + Y - C + A]$

Here, V = valence shell electrons of the central metal, Y = number of monovalent atom
C = total positive charge on mulecule and A = total negative charge on molecule
For the 2, 3, 4, 5, 6 and 7 value of H, the hybridisation is respectively sp, sp^2, sp^3, sp^3d, sp^3d^2 and sp^3d^3.

Types of Hybridisation

Number of electron pairs around central atom and hybridisation	2 (sp^2)	3 (sp^2)	4 (sp^3)	5 (sp^3d)	6 (sp^3d^2)	7 (sp^3d^3)
Shape	Linear	Trigonal planar	Tetrahedral	Trigonal bipyramidal	Octahedral	Pentagonal bipyramidal
Bond angles	X—A—X, 180°	120°	109.5°	90°, 120°	90°	72°, 90°
Examples	BeF_2, $HgCl_2$	BF_3	CF_4, CH_4, NH_4^+	PF_5, PCl_5	SF_6	IF_7

Valence Shell Electron Pair Repulsion Theory (VSEPR Theory)

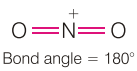
Presence of lone pairs distort the normal shape due to lone pair-lone pair and lone pair-bond pair repulsion. Such distortions can be explained by valence shell electron pair repulsion (VSEPR) theory. The main postulates of this theory are :

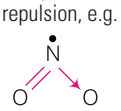
1. In polyatomic molecules the least electronegative atom is called central atom, with which all other atoms are linked.
2. The geometry of the molecule depends upon the total number of valence electron pairs (either bond pair or lone pair) around the central atom and the repulsions between these electron pairs.
3. The repulsion among pairs increases as
$bp - bp < bp - lp < lp - lp$.

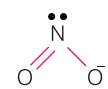
REMEMBER

Presence of lone pair of electrons greatly affect the bond angle. Some such examples are given below :

1. As the number of lone pairs of electrons increases, bond angle decreases.
2. pi (π) bond do not affect the stereochemistry of a molecule. However, multiple bond orbitals, repel other orbitals more strongly than single bond orbital, increasing the bond angle.
3. A lone pair and double bond repulsion is much greater than a lone electron and double bond repulsion, e.g.


Bond angle = 180°
(No lone pair)

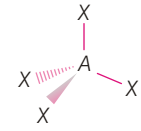

Bond angle = 134°
(A lone electron)

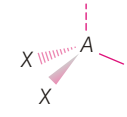

Bond angle = 115°
(A lone pair)

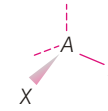
4. The bond angle of PF_3 > PCl_3. The PF_3 molecule has lone pair of electrons on F-atom and P has vacant d-orbitals. The small size of F-atom leads to $p\pi$-$d\pi$ bonding in PF_3.
The double bond formation increases bond pair-bond- pair repulsion to result in an increase in bond angle in PF_3. In PCl_3, the Cl-atom being larger in size does not show $p\pi$-$d\pi$ bonding.

Geometries adopted by molecules based on the trigonal planar, tetrahedral, trigonal bipyramidal and octahedral geometries containing zero, one or two lone pairs are given below. For those containing lone pairs, the observed shape generally differs a little from that shown because of the greater repulsive effect of the lone pairs. The only exception is square planar.

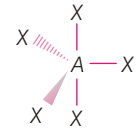
1. Structure based on trigonal planar is only bent (with one lone pair).
2. Structures based on tetrahedral geometry
(Nolonepairs)

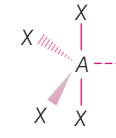

Tetrahedral(0 *lp*)

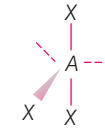

Trigonalpyramidal(1 *lp*)


Bent (2 *lp*)

3. Structures based on trigonal bipyramidal geometry


Trigonal bipyramidal (0 *lp*)


Disphenoidal or *see-saw* (1 *lp*)


T-shaped (2 *lp*)

4. Structures based on octahedral geometry

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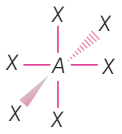

Octahedral (0 *lp*)

Square pyramidal (1 *lp*)

Square planar (2 *lp*)

Note If within a molecule, we keep the central atom (having lone pair) same and changes the surrounding atoms that have increased value of electronegativity, the bond angle will decrease provided no other factors like size and back bonding play any role. If surrounding atoms are kept same and electronegativity of central atom (have lone pair) increases bond angle increases.

Best Practice SHOTS

16. Which of the following statement is incorrect?
(a) I_3^- molecule has bent shape
(b) PCl_5 exists but NCl_5 does not exist
(c) SeF_4 and CH_4 have same shape
(d) $p\pi$ - $d\pi$ bonds are present in SO_2

17. The hybridisation of P, when PCl_5 dissolved in water is
(a) sp^3d^2 (b) sp^3 (c) sp^3d (d) sp^2
Hint $PCl_5 + 4H_2O \rightarrow H_3PO_4 + 5HCl$

18. The types of hybrid orbitals of nitrogen in NO_2^+, NO_3^- and NH_4^+ respectively are expected to be
(a) *sp*, sp^3 and sp^2 (b) *sp*, sp^2 and sp^3
(c) sp^2, *sp* and sp^3 (d) sp^2, sp^3 and *sp*

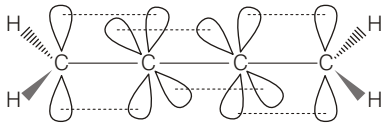
19. In which of the following molecule/ion all the bonds are not equal?
(a) XeF_4 (b) BF_4^-
(c) C_2H_4 (d) SiF_4

20. The VSEPR model is based on the
(a) number of bonded pairs of electrons around the central atom
(b) number of bonded and lone pairs of electrons around the central atom
(c) number of lone pairs of electrons around the central atom
(d) number of protons around the central atom

21. Select the pair of compounds in which both have different hybridisation but have same molecular geometry.
(a) BCl_3, PCl_3 (b) PCl_3, NCl_3
(c) BF_3, BrF_3 (d) ICl_2^-, $BeCl_2$

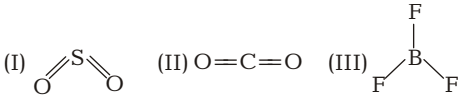
22. Nodal planes of π-bonds in $CH_2=C=C=CH_2$ located in
(a) two in molecular plane and one in a plane perpendicular to molecular plane which bisects C—C σ-bonds at right angle
(b) one in molecular plane and two in plane perpendicular to molecular plane which contains C—C σ-bonds
(c) two in molecular plane and one in a plane perpendicular to the molecular plane which contains C—C σ-bond
(d) All the above are in molecular plane

Hint



23. $sp^3 + d_{x^2-y^2} \rightarrow sp^3 d_{x^2-y^2}$. Now the shape becomes
(a) hexahedral (b) square pyramidal
(c) square planar (d) trigonal bipyramidal

24. Which will show resonance?



(a) I and II (b) I and III (c) II and III (d) I, II and III

25. H – C – O^-, The correct order of bond length *a* and *b* is

(a) $a < b$ (b) $a > b$ (c) $a = 2b$ (d) $a = b$

26. Molecular shape of SF_4, CF_4 and XeF_4 are
(a) the same, with 2, 0 and 1 lone pair of electrons respectively
(b) the same, with 1, 1 and 1 lone pairs of electrons respectively
(c) different, with 0, 1 and 2 lone pairs of electrons respectively
(d) different, with 1, 0 and 2 lone pair of electrons respectively

CHEMISTRY IN action

A new form of real gold, almost as light as air

A nugget of real 20 carats gold, so light that it does not sink in a cappuccino, floating instead on the milk foam, what sounds unbelievable has actually been accomplished by researchers who have created a new type of foam made of real gold. It is the lightest form ever produced of the precious metal: a thousand times lighter than its conventional form and yet it is nearly impossible to tell the difference with the naked eye. But in contrast to its conventional form, it is soft and malleable by hand. It consists of 98 parts air and only two parts of solid material. Of this solid material, more than four-fifths are gold and less than one-fifth is milk protein fibrils. This corresponds to around 20 carat gold. There are many possible applications, where, gold is currently being used. Applications in watches and jewelry are only one possibility. Another application demonstrated by the scientists is chemical catalysis: since the highly porous material has a huge surface, chemical reactions that depend on the presence of gold can be run in a very efficient manner. The material could also be used in applications where light is absorbed or reflected. Finally, the scientists have also shown how it becomes possible to manufacture pressure sensors with it.

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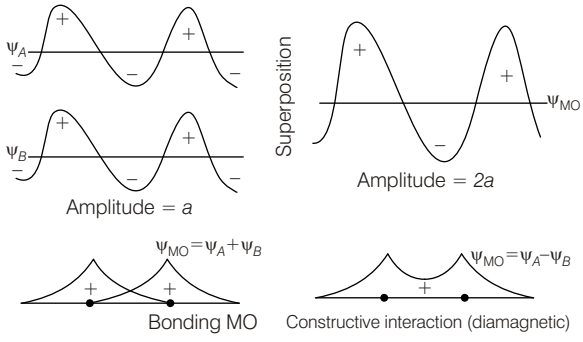
MOT, COORDINATE BOND, METALLIC BONDING AND HYDROGEN BONDING

Molecular Orbital Theory (MOT)

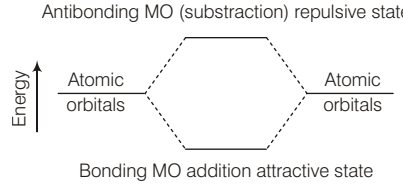
The molecular orbital theory (MOT) of chemical bonding is based on Schrodinger wave interpretation of electrons.

- According to this theory, a molecule is supposed to have orbitals of varying energy levels in the same way as an isolated atom has. These orbitals of molecule are called molecular orbitals. The quantised molecular orbitals surround all the nuclei of bonded atoms and are formed by the coalescence of individual atomic orbitals of atoms present in the molecule. Thus, orbitals of atoms loose their individual identity.
- To yield quantitative picture of molecular orbitals in a molecule, we use a quantum method named is linear combination of atomic orbitals (LCAOs). When atomic orbitals or lobes of orbitals with same wave function (ψ) combine, the result is constructive interaction while when atomic orbitals or lobes of orbitals with opposite wave function (ψ) combine, the result is destructive interaction.
- Constructive interaction of orbitals give rise to orbitals of lower energy, called bonding orbitals or HOMOs (Highest Occupied Molecular Orbitals) as electrons prefer to stay in these orbitals due to their lower energy than atomic orbitals.



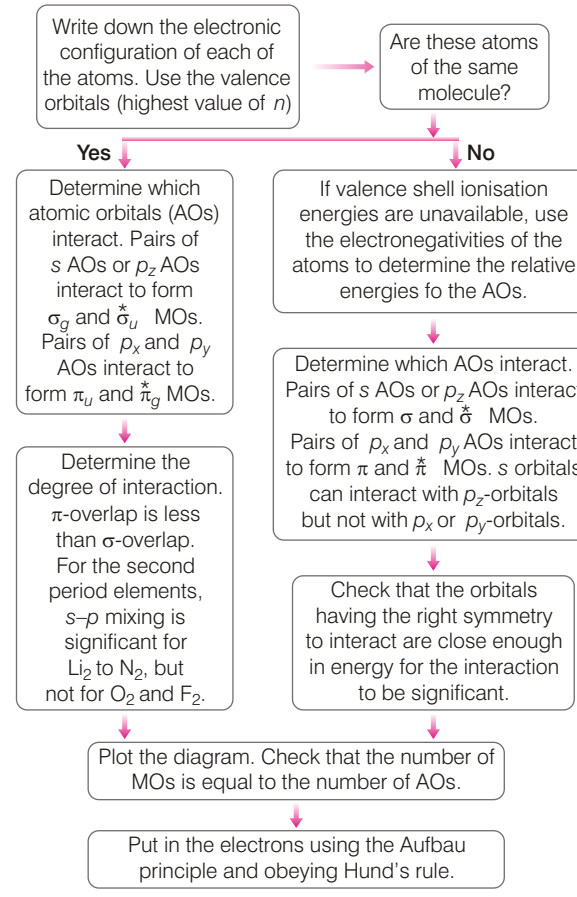
- Destructive interaction the other hand give rise to orbitals of higher energy, called anti-bonding orbitals or LUMOs (Lowest or Unoccupied Molecular Orbitals) as electrons do not prefer them due to their higher energy than atomic orbitals.

Energy Level Diagram for Molecular Orbitals



Thus, the probability of finding electrons in bonding MOs is much higher as compared to respective MOs.

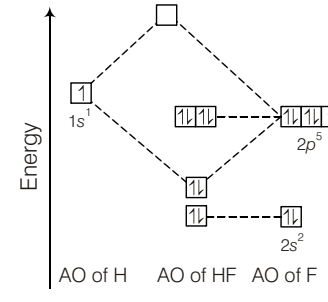
How to Construct ELD for a Diatomic Molecule?



CHEMISTRY CONCENTRATE

FORMATION AND STABILITY OF HETERONUCLEAR MOLECULES

As the energies of input atomic orbitals will not be same, which will give rise to unequal splitting of MO's. Bonding orbitals will have more character of stable AO while antibonding orbitals will have more character of unstable combining AO. Only AO's of comparable energies can be combined to form MO's.



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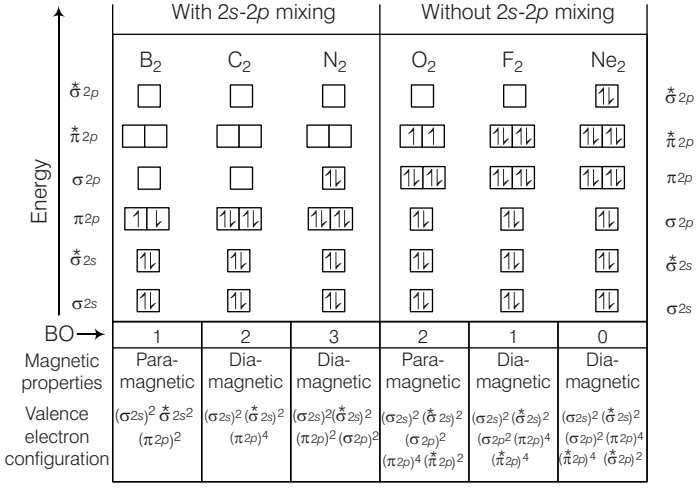
Facts

- 1*s* orbital of H is too high in energy that it cannot interact with 1*s* or 2*s* orbital of fluorine.
- It interact with only one 2*p* orbital having symmetry to form MO 's indicated in the figure above.
- Out of total 8 valence electrons of HF molecule, only two are in delocalised MO's. Finally, we can sum up the MO diagram of molecules from $B_2 \rightarrow Ne_2$ in the following table:



Conclusion

- Ne_2 has zero bond length and bond energy because bond is not formed between Ne-atom,
- B_2 and O_2 are paramagnetic as they have unpaired electrons while C_2, N_2 and F_2 are diamagnetic as they do not have unpaired electrons.
- As bond order increases bond energy also increases. Hence, N_2 has highest value of bond energy.
- Bond length decreases as bond order increases. Hence, B_2 shows highest value of bond length.
- Although O_2 and F_2 have same bond order as C_2 and B_2 but these have lower bond energy and bond length than B_2 and C_2 due to their high value of electronegativity.

Filling of Electrons in Molecular Orbitals

The energy levels of molecular orbitals have been determined experimentally from spectroscopic data, for homonuclear diatomic molecules of the second row elements of the periodic table. The increasing order of energies of molecular orbitals for O_2 and F_2 molecules is given as $\sigma 1s < \overset{*}{\sigma} 1s < \sigma 2s < \overset{*}{\sigma} 2s < \sigma 2p_z$

$< \pi 2p_x \approx \pi 2p_y < \overset{*}{\pi} 2p_x \approx \overset{*}{\pi}\, 2p_y < \overset{*}{\sigma}\, 2p_z$

However, for remaining molecules,

i.e. Li_2, Be_2, B_2, C_2, N_2 the order is

$\sigma 1s < \overset{*}{\sigma} 1s < \ \sigma\, 2s < \overset{*}{\sigma} 2s < \pi 2p_x \approx \pi 2p_y < \sigma 2p_z$

$< \pi^* 2p_x \approx \pi^* 2p_y \ < \sigma^* 2p_z$

i.e. here energy of $\pi 2p_x \approx \pi 2p_y$ is less than the energy of $\sigma 2p_z$ molecular orbital.

Bond Order

$$\text{Bond order} = \frac{N_b - N_a}{2}$$

here, N_b = number of electrons in bonding orbitals

N_a = number of electrons in anti-bonding orbitals

- The stability of a molecule can be determined by its bond order as :
  1. A positive bond order means a stable molecule.
  2. A negative or zero bond order means an unstable molecule.
  3. Bond order values 1,2 and 3 corresponds to single, double and triple bond respectively.

  $$\text{Bond order } \mu \frac{1}{\text{Bond length}}$$
- Magnetic nature of molecules can also be determined by molecular orbitals as:
  1. If all orbitals are fully occupied, the substance is diamagnetic.
  2. If one or more molecular orbitals is/are singly occupied, the substance is paramagnetic.

Bonding in Some Homonuclear Diatomic Molecules

(a) **H_2 molecule**

Electronic configuration $\sigma 1s^2$

Bond order = 1

(b) **He_2 molecule**

Electronic configuration $\sigma 1s^2$, $\overset{*}{\sigma} 1s^2$

Bond order = 0

(c) **Li_2 molecule**

Electronic configuration $\sigma 1s^2$, $\overset{*}{\sigma} 1s^2$, $\sigma 2s^2$

Bond order = 1

(d) **C_2 molecule**

Electronic configuration

$\sigma 1s^2$, $\overset{*}{\sigma}\, 1s^2$, $\sigma 2s^2$, $\overset{*}{\sigma}\, 2s^2$, $\pi 2p_x^2 \approx \pi 2p_y^2$

Bond order = 2

(e) **O_2 molecule**

Electronic configuration

$\sigma 1s^2$, $\overset{*}{\sigma}\, 1s^2$, $\sigma 2s^2$, $\overset{*}{\sigma}\, 2s^2$, $\sigma 2p_z^2$,

$\pi 2p_x^2 \approx \pi 2p_y^2$, $\overset{*}{\pi} 2p_x^1 \approx \pi 2p_y^1$

Bond order = 2

(f) **F_2 molecule**

Electronic configuration

$\sigma 1s^2$, $\overset{*}{\sigma}\, 1s^2$, $\sigma 2s^2$, $\overset{*}{\sigma}\, 2s^2$, $\sigma 2p_z^2$,

$\pi 2p_x^2 \approx \pi 2p_y^2$, $\overset{*}{\pi}\ 2p_x^2 \approx \overset{*}{\pi}\ 2p_y^2$

Bond order = 1

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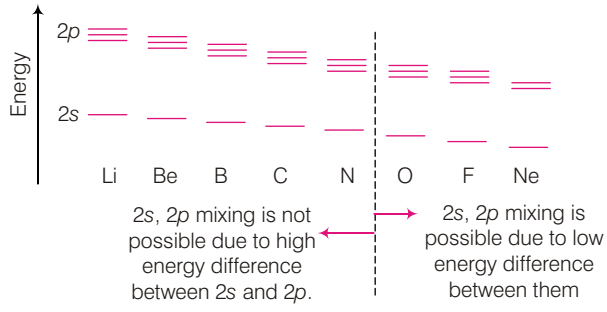
s-p Mixing

It can be seen due to low energy difference between 2*s* and 2*p* orbitals.
(Mainly from $B_2 \rightarrow N_2$) due to which energy of $\sigma 2p$ bonding MO increases.

Why the energy of 2*s* and 2*p* vary with *Z* (atomic number)?

As *Z* increases, shielding of outermost orbit decreases as effective nuclear charges (Z_{eff}) increases along a period making 2*s* orbital more sable continuously (shielding/penetration effect).

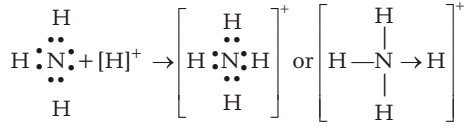
Following diagram shows the variation of energy of 2*s* orbital and growing energy difference with *Z* between 2*s* and 2*p* orbitals.



Coordinate Bond

Coordinate **covalent bond** or **dative bond** is a special type of covalent bond, in which shared electron pair is donated by one atom (called donor) and shared by both the atoms (the other atom being called acceptor), e.g.

Fomation of NH_4^+

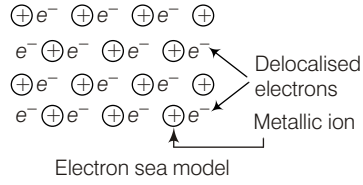


Metallic Bonding

The particular type of bonding which holds the metal atoms together in a metal crystal is called metallic bonding. Different models to explain the nature of metallic bonding, are as follow:

Electron Sea Model

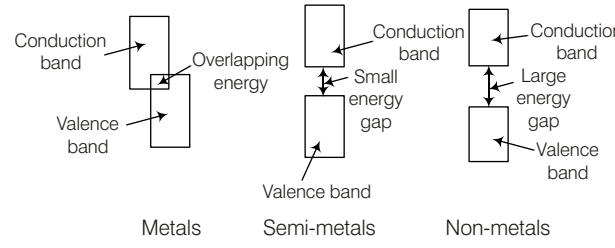
- According to this, a metal is regarded as a group of positive metal ions packed together as closely as possible in a regular geometric pattern and immersed in a sea of electrons which move freely in the vacant valence orbitals.
- The attractive force that binds the metal ions to the mobile electrons is called metallic bond.



Electron sea model

Band Model

- The band model of metallic bonding is based on molecular orbital theory. According to this theory, a metal lattice has extremely large number of atoms. The atomic orbitals of these atoms overlap together due to similar symmetry and similar energy resulting to the formation of energy bands. The arrangement of electrons in the different energy bands determines the characteristic of a metal.
- The highest occupied energy band is called the **valence band** while the lowest unoccupied energy band is called **conduction band** . The properties of various elemental solids can be explained by the gap present between the top of valence band and the bottom of conduction band, called **energy gap** (E_g). In the case of metals, semi-metals and non-metals the valence and conduction bands can be seen as:



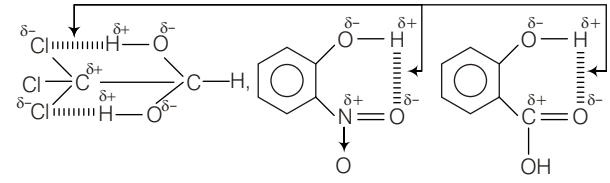
Hydrogen Bonding

It is an attractive force exerted between a hydrogen atom and a strong electronegative atom (F, O, N or C).

Types of Hydrogen Bonding

(a) **Intramolecular H-bonding** It is seen in a single molecule and when this type of H-bonding leads to the linking of two groups in such a way that a ring like structure is formed, the effect is also called chelation, e.g.

Intramolecular hydrogen bonding



Butterfly structure of chloral hydrate ($CCl_3CH(OH)_2$) | *o*-nitrophenol | Salicylic acid (*ortho*-hydroxy benzoic acid)

Molecules with intramolecular H-bonding are known to have lower boiling and melting points.

(b) **Intermolecular H-bonding** It occurs between two or more molecules of similar or different compounds,

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- The intermolecular H-bonding is found to be responsible for high melting and boiling points of compounds in which it is seen.
- Certain organic compounds like alcohols show miscibility with polar solvents like water. It is also attributed to intermolecular H-bonding between alcohol and water molecules.

Nature and Importance of H-bonding

1. H-bond is simply dipole-dipole attraction between oppositely partially charged ends.
2. H-bond never involves more than two atoms.
3. Bond energy of H-bond is of the order of 3 –10 kcal mol^{-1}, i.e. about 1/10 of covalent bond.
4. As the electronegativity difference of H and other atom to which it is covalently bonded increases, the strength of H-bond increases, e.g.

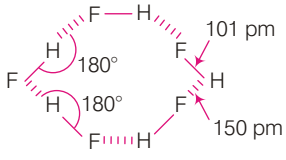
   H¾F > H¾O > H¾N > H¾Cl
5. All the three atoms X ¾ H ¾ X lie in one plane.

Effects of H-Bonding

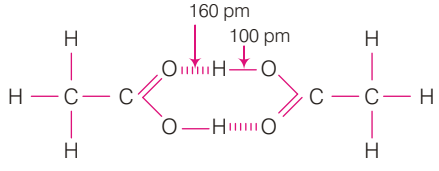
(a) **High boiling point of water** Due to polar nature of H_2O, there is association of water giving a liquid state of abnormally high boiling point. Actually, in water, one water molecule is joined to four water molecules (two with H-atom and other two with O-atoms.). Thus, coordination number of water molecule in water is four.

(b) **Low density of ice as compared to water** When ice is formed from liquid water; some air gap are formed (in tetrahedral packing of water molecules). Due to this, volume of ice is greater than liquid water and thus, ice is lighter than water. In another word, we can say that density increases but only upto 4°C, after this intermolecular H-bonding between water molecules breaks, hence volume increases and hence, density decreases. Thus, water has maximum density at 4°C.

(c) **Pentagonal arrangement of HF** In the gaseous state, several polymeric forms of HF molecules exist in which the monomers are held together through H-bonding. A pentagonal arrangement of HF molecules as shown



(d) **Dimerisation of carboxylic acids** They dimerises in gaseous state due to H-bonding.



van der Waals' Forces

van der Waals' forces are very short lived intermolecular attractive forces which are believed to exist between all kinds of molecules when they are sufficiently close to each other.
Types of van der Waals' forces :

(a) **Dipole-dipole interactions** When polar molecules are brought nearer to each other, they orient themselves in such as way that positive end of one dipole attracts the negative end of other dipole and *vice-versa* as.

- These forces are strongest of all van der Waals' forces and are called Keesom forces. The intensity of these forces is generally hampered by an increase in temperature.

(b) **Ion-induced dipole interactions** Polar molecules are attracted towards ions and this interaction between ions and dipoles is called ion dipole interaction. Ions however, can attract neutral molecules also and have the ability of causing polarity in them. Such interactions are called ion-induced dipole interaction.

(c) **Dipole-induced dipole interactions** When a dipole comes near the non-polar molecule it can induce polarity in non-polar molecule resulting to dipole-induced dipole interactions.

(d) **Instantaneous dipole induced dipole interactions** Even non-polar molecules in themselves are polarised temporally due to displacement of electron cloud with respect to nucleus (instantaneously). Such an instantaneous polar dipole when interact with non-polar molecule, the result is seen in the form of instantaneous dipole induced dipole interaction.

Notice Board

VITEEE 2016

VIT University will conduct VIT Engineering Entrance Exam (VITEEE) 2016 for granting admissions to various undergraduate engineering programmes. Admissions to its two campuses, Chennai and Vellore, will be purely on the basis of the marks secured in the VITEEE 2016.

VITEEE 2016 Exam Pattern

The Paper will have 125 questions in total with 40 questions each in Physics, Chemistry, Maths/ Biology and 5 questions in English. No negative marking will be there in the question paper. All questions will be of objective type and as per the exam pattern. Each question will be followed by four alternative answers and the candidates have to select the right option. Candidates will be given two and half hours to complete the online test. There will be no negative marking for wrong answers.

VITEEE 2016 Important Dates

Complete schedule of VITEEE 2016 will be announced by the university later. In the meantime, aspirants can check here other important dates at official website.

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Best Practice SHOTS

27. The $\overset{*}{\pi}$ molecular orbital in ethene is
(a) symmetric under inversion and antisymmetric under reflection about the plane of the molecule
(b) antisymmetric under inversion and symmetric under reflection about the plane of the molecule
(c) symmetric under inversion and symmetric under reflection about the plane of the molecule
(d) antisymmetric under inversion and antisymmetric under reflection about the plane of the molecule

28. Which of the following order of energy of molecular orbitals of N_2 is correct?
(a) $(\pi 2p_y) < (\sigma 2p_z) < (\pi^* 2p_x) \approx (\pi^* 2p_y)$
(b) $(\pi 2p_y) > (\sigma 2p_z) > (\pi^* 2p_x) \approx (\pi^* 2p_y)$
(c) $(\pi 2p_y) < (\sigma 2p_z) > (\pi^* 2p_x) \approx (\pi^* 2p_y)$
(d) $(\pi 2p_y) > (\sigma 2p_y) < (\pi * 2p_x) \approx (\pi^* 2p_y)$

29. Which of the following options represents the correct bond order?
(a) $O_2^- > O_2 > O_2^+$ (b) $O_2^- < O_2 < O_2^+$
(c) $O_2^- > O_2 > O_2^+$ (d) $O_2^- < O_2 < O_2^+$

30. Which of the following statements is not correct from the view point of molecular orbital theory?
(a) Be_2 is not a stable molecule
(b) He_2 is not stable but He_2^+ is expected to exist
(c) Bond strength of N_2 is maximum amongst the homonuclear diatomic molecules belonging to the second period
(d) The order of energies of molecular orbitals in N_2 molecule is
$\sigma 2s < \overset{*}{\sigma} 2s < \sigma 2p_z < (\pi 2p_x \approx \pi 2p_y) < (\overset{*}{\pi} 2p_x = \overset{*}{\pi} 2p_y) < \overset{*}{\sigma} 2p_z$

31. Hydrogen bonds are formed in many compounds e.g. H_2O, HF, NH_3 etc. The boiling point of such compounds depends to a extent on the strength of hydrogen bond and the number of hydrogen bonds. The correct decreasing order of the boiling points above compounds is
(a) HF > H_2O > NH_3 (b) H_2O > HF > NH_3
(c) NH_3 > HF > H_2O (d) NH_3 > H_2O > HF

32. Among the following orbitals of a diatomic molecule, the bonding one is
(a) $2\sigma_u$ (b) $1\pi_u$
(c) $1\sigma_u$ (d) $1\pi_u$
Hint σ-bonding — gerade (*g*)
$\overset{*}{\sigma}$-bonding — ungerade (*u*)
π-bonding — ungerade (*u*)
$\overset{*}{\pi}$-bonding — gerade (*g*)

33. The common features among the species CN^-, CO and NO^+ are
(a) isoelectronic and weak field ligand
(b) bond order three and isoelectronic
(c) bond order three and weak field ligand
(d) bond order two and π-acceptors

34. N_2 and O_2 are converted into monocations. Which of the following statement is wrong?
(a) In O_2, paramagnetism decreases
(b) $N_2^{\oplus}$ becomes diamagnetic
(c) In N_2, the N—N bond weakers
(d) In O_2, the O—O bond order increases

35. In which of the following ionisation processes, the bond order has increased and the magnetic behaviour has changed?
(a) $C_2 \rightarrow C_2^+$
(b) $NO \rightarrow NO^+$
(c) $O_2 \rightarrow O_2^+$
(d) $N_2 \rightarrow N_2^+$

36. In which of the following pairs of molecules/ions both the species are not likely to exits?
(a) H_2^+, He_2^{2-} (b) H_2^-, He_2^{2-}
(c) H_2^{2+}, He_2 (d) H_2^-, He_2^{2+}

Hint Species having zero or negative bond order do not exist.

37. The correct order of increasing C—O bond length of CO, CO_3^{2-}, CO_2
(a) $CO_3^{2-} < CO_2 < CO$
(b) $CO_2 < CO_3^{2-} < CO$
(c) $CO < CO_3^{2-} < CO_2$
(d) $CO < CO_2 < CO_3^{2-}$

38. The cyanide ion, CN^- and N_2 are isoelectronic, but in contrast to CN^-, N_2 is chemically inert, because of
(a) low bond energy
(b) absence of bond polarity
(c) unsymmetrical electron distribution
(d) presence of more electrons in bonding orbitals

39. Nitric oxide has the electronic configuration is
$\sigma 1s^2, \overset{*}{\sigma} 1s^2, \sigma 2s^2, \overset{*}{\sigma} 2s^2, \sigma 2p_z^2, \pi 2p_x^2 = \pi 2p_y^2, \overset{*}{\pi} 2p_x^1 = \overset{*}{\pi} 2p_y^0$
which of the following statement is correct?
(a) On ionisation to form NO^+, its bond order increases and bond length decreases
(b) On ionisation to form NO^+, its bond order decreases and bond length decreases
(c) On ionisation to from NO^+, its bond decreases and bond length increases
(d) On ionisation to form NO^+, its bond order increases and bond length decreases

40. Concept of bond order in the molecular orbital theory depends on the number of electrons in the bonding and antibonding orbitals. The bond order
(a) is a non-zero quantity
(b) can assume any positive value, including zero
(c) can have a negative value
(d) has always on integral value

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Answers

1. (b)	**2.** (b)	**3.** (b)	**4.** (a)	**5.** (c)	**6.** (a)	**7.** (b)	**8.** (c)	**9.** (a)	**10.** (b)
11. (c)	**12.** (c)	**13.** (d)	**14.** (c)	**15.** (a)	**16.** (c)	**17.** (b)	**18.** (b)	**19.** (c)	**20.** (b)
21. (d)	**22.** (c)	**23.** (b)	**24.** (d)	**25.** (d)	**26.** (d)	**27.** (a)	**28.** (a)	**29.** (b)	**30.** (d)
31. (b)	**32.** (b)	**33.** (b)	**34.** (b)	**35.** (b)	**36.** (c)	**37.** (d)	**38.** (b)	**39.** (d)	**40.** (b)

MASTER STROKES

1. In the compound *M*—O—H, the *M*—O bond will be broken if

(a) Δ(EN) of *M* and O = Δ(EN) of O and H
(b) Δ(EN) of *M* and O > Δ(EN) of O and H
(c) Δ(EN) of *M* and O < Δ(EN) of O and H
(d) cannot be predicted according to Δ(EN) data

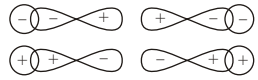
Hint More will be electronegativity difference between atoms, more will be ionic character.

2. Which of the following statements is correct about N_3^- ion?

(a) It is isoelectronic with CN^- and is linear like CO_2
(b) The three $2p_y$ orbitals form three three-centre π molecular orbital
(c) Six electrons are used for the two σ-bonds
(d) All of the above

Hint If the bonding and non-bonding electrons are assumed to use the 2*s* and $2p_x$ orbitals, this leaves six atomic orbitals for π-bonding.

3. Which of the following are the correct molecular orbitals for C_2H_2?

I.
II.
III. 
IV.

(a) I and IV *(b)* II and III
(c) III and IV *(d)* All of these

4. Amongst the following elements whose electronic configuration are given below, the one having the highest ionisation enthalpy is

(a) [Ne] $3s^2 3p^1$ *(b)* [Ne] $3s^2 3p^3$
(c) [Ne] $3s^2 3p^2$ *(d)* [Ar] $3d^{10} 4s^2 4p^3$

5. NO_2 gas is paramagnetic at room temperature. On cooling below 0°C, it becomes diamagnetic. The reason behind this change of property is

(a) NO_2 becomes amorphous
(b) NO_2 becomes liquid
(c) NO_2 becomes N_2O_4
(d) NO_2 becomes solid

6. Consider the electronic states of an atom $A: 1s^2 2s^2 2p^6 3s^1$ and $B: 1s^2\ 2s^2\ 2p^6\ 4s^1$. Which one of the following statement is false?

(a) *B* represents and excited state of the atom
(b) more energy is required to remove an electron from *B* than from *A*
(c) Energy is required to change *A* into *B*
(d) *A* represents an alkali metal

7. Among the following species, identify the isostructural pairs.

$$NF_3, NO_3^-, BF_3, H_3O^+, N_3H$$

(a) [NF_3, NO_3^-] and [BF_3, H_3O^+]
(b) [NF_3, N_3H] and [NO_3^-, BF_3]
(c) [NF_3, H_3O^+] and [NO_3^-, BF_3]
(d) [NF_3, H_3O^+] and [N_3H, BF_3]

8. Polarity in a molecule and hence the dipole moment depends primarily on electronegativity of the constituent atoms and shape of a molecule. Which of the following has the highest dipole moment?

(a) CO_2 *(b)* HI *(c)* H_2O *(d)* SO_2

9. The electronegativity order of *X*, *Y*, *Z*, is *X* < *Y* < *Z*. Then which is correct for $X\begin{matrix}Y\\Z\end{matrix}$ type molecule ?

(a) *X* will have two opposite charge
(b) Bond lengths of *X*—*Y* and *X*—*Z* are differents
(c) bond moments of *X*—*Y* and *X*—*Z* are some
(d) All of the above

10. Which of the following statement is not correct?

(a) F_2^+ has a higher bond order than F_2
(b) O_2^+ has a higher bond order than O_2
(c) N_2^- has a lower bond order than N_2
(d) NO^+ has a lower bond order than NO

Answers

1. (b)	**2.** (b)	**3.** (c)	**4.** (b)	**5.** (c)	**6.** (b)	**7.** (c)	**8.** (c)	**9.** (b)	**10.** (d)

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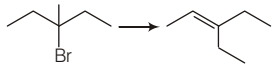
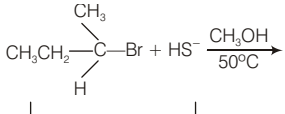
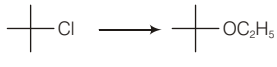
JEE MAIN PREP UP

Mock Questions with Complete Solutions

1. Match the following (Column I) which represents reactions to the (Column II) representing reaction conditions.

Column I	Column II
A. $(CH_3CH_2)_3CBr \xrightarrow[25^\circ C]{CH_3OH}$	p. Strong base, high temperature.
B. 	q. Weak base and a poor nucleophile, first order reaction.
C. 	r. Low temperature, S_N1.
D. 	s. Strong nucleophile, weak base, second order reaction.

	A	B	C	D		A	B	C	D
(a)	p	q	r	s	*(b)*	q	p	s	r
(c)	r	p	q	s	*(d)*	r	p	s	q

2. Enthalpies of hydrogenation of ethylene (C_2H_4) and benzene (C_6H_6) have been measured, when all reactants and products are gases.

$$C_2H_4 + H_2 \rightarrow C_2H_6;\ \Delta H = -32.7 \text{ kcal}$$

$$C_6H_6 + 3H_2 \rightarrow C_6H_{12};\ \Delta H = -49.2 \text{ kcal}$$

The resonance energy of benzene is

(a) – 49.2 kcal *(b)* 49.2 kcal *(c)* 48.9 kcal *(d)* – 48.9 kcal

3. Match the following columns.

Column I (Metal)		Column II (Ore)		Column III (Method of extraction)	
A.	Na	p.	Millerite	w.	By reduction of NiO with Co
B.	Fe	q.	Chromite	x.	Br reduction of Fe_2O_3 with Co
C.	Cr	r.	Haematite	y	By reduction of Cr_2O_3 with Al
D.	Ni	s.	Rock salt	z.	By electrolysis of fused NaCl + $CaCl_2$

	A	B	C	D
(a)	s-z	r-x	p-w	q-y
(b)	s-z	r-x	q-y	p-w
(c)	r-z	q-z	q-y	s-w
(d)	s-x	r-z	q-w	p-y

4. Copper could reduce zinc ions if the resultant copper ions can be kept at sufficiently low concentration by the formation of an insoluble salt. The maximum concentration of Cu^{2+} in solution if the reaction is to occur when Zn^{2+} in 1.00 molar is ($E^\circ = -1.10$ V)

(a) 5.23×10^{-38} M
(b) 7.12×10^{-36} M
(c) 6.31×10^{-38} M
(d) 4.29×10^{-36} M

5. Which of the following statements is incorrect?

(a) Vitamins are not stored in the body but are continuously produced
(b) Hormones are produced in the endocrine glands
(c) Vitamins are not produced in the body but have to be supplied in food
(d) Secondary structure of proteins refers to the conformation which the polypeptide chain assume as a result of H-bonding

6. Which of the following statements are correct?

I. $[Co(NH_3)_6]^{3+}$ is an inner orbital complex while $[Ni(NH_3)_6]^{2+}$ outer orbital complex.

II. Magnetic moment of $[Fe(H_2O)_6]^{2+}$ is 6.9 BM, while that of $[Fe(CN)_6]^{4-}$ in 4.9 BM.

III. $[Fe(CN)_6]^{3-}$ is weakly paramagnetic while $[Fe(CN)_6]^{4-}$ diamagnetic.

IV. Both $[NiCl_4]^{2-}$ and $[Ni(CO)_4]$ are tetrahedral but former is paramagnetic while later is diamagnetic.

(a) I, II and III *(b)* I, II and IV
(c) II, III and IV *(d)* I, III and IV

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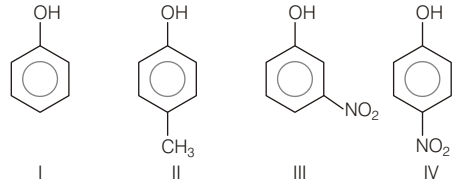
7. Arrange the following compounds in the increasing order of basicity.



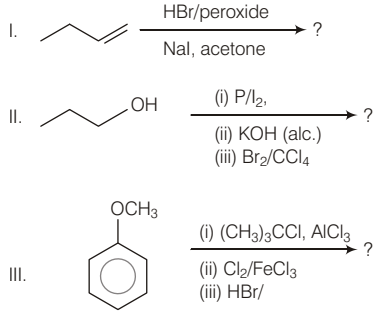
(a) III > IV > I > II
(b) I > IV > III > II
(c) IV < III < I < II
(d) II < I < III < IV

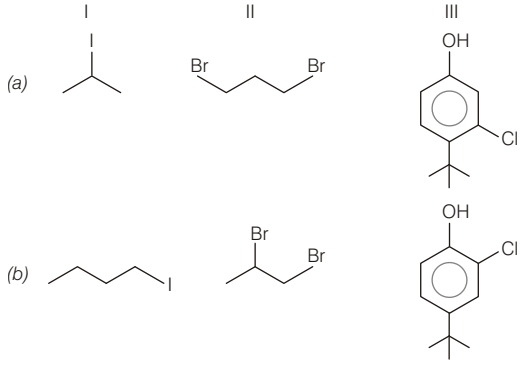
8. A buffer solution was prepared by dissolving 0.050 mole of formic acid and 0.060 mole of sodium formate in enough water to make 1.0 L of solution. K_a for formic acid is 1.80×10^{-4}. Which of the following statements is/are correct?

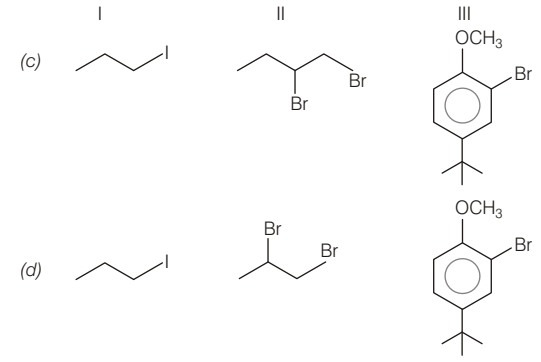
I. The pH of the solution was 3.83.
II. If this solution was diluted to 10 times of its volume, the pH will be 2.85.
III. If the solution in (b) was dilute to 10 times of its volume, the pH will be 3.99.

(a) I and II
(b) I and III
(c) Only I
(d) II and III

9. Identify the major product.







10. Which of the following statements are correct?

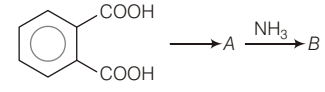
I. In the extraction of Ag from $[Ag(CN)_2]^-$, Zn is used in place of Cu.
II. When NH_4OH is added to copper sulphate solution, a deep blue colour appears.
III. $AgNO_3$ is called Lunar caustic.
IV. $AgNO_3$ gives white precipitate with NaCl but not with CCl_4

(a) I and II *(b)* I, II and III *(c)* II, III and IV *(d)* All of these

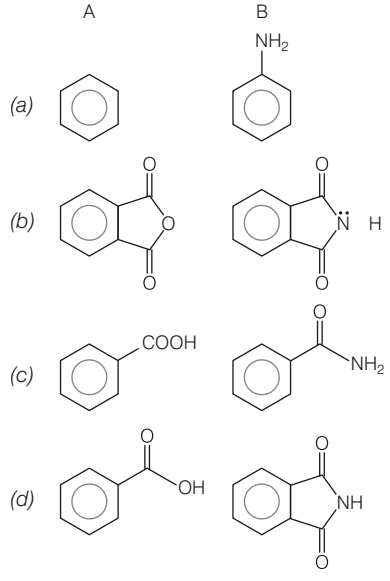
11. Iron crystallises in several modification. At about 910° C, the body-centred cubic α-form undergoes a transition to the face-centred cubic γ-form. Assuming that the distance between nearest neighbours is same in both forms at the transition temperature, the ratio of the density of γ-iron to that of α-iron at the transition temperature is

(a) 2.0 *(b)* 1.09 *(c)* 2.09 *(d)* 1.90

12.



Identify the products *A* and *B* respectively



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13. In the isoelectronic series VO_4^{3-}, CrO_4^{2-} and MnO_4^-, all members have intense charge transfer transitions. The incorrect statement is

(a) The charge on metal nucleus increases in the order $VO_4^{3-} < CrO_4^{2-} < MnO_4^-$

(b) Charge transfer transitions are attributed to excitations of electrons from ligand to metal

(c) MnO_4^- exhibits charge transfer at shortest wavelength among the three

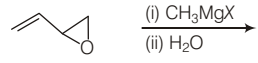
(d) The wavelength of transitions increases in order $VO_4^{3-} < CrO_4^{2-} < MnO_4^-$

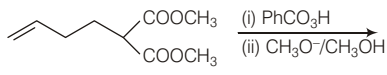
14. In a basal metabolism measurement timed at 7.00 min, a patient exhaled 62.5 L of air, measured over water at 20° C.

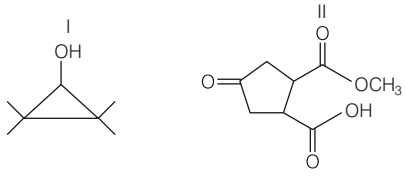
The vapour pressure of water at 20° C is 27.5 torr. The barometric pressure was 740 torr. The exhaled air analysed 15.64 vol % of oxygen and the inhaled air 25.45 vol% of oxygen, both on a dry basis. Neglecting any solubility of the gases in water and any difference in the total volumes of inhaled and exhaled air, the rate of oxygen consumption by the patient in mL (STP) per minute is

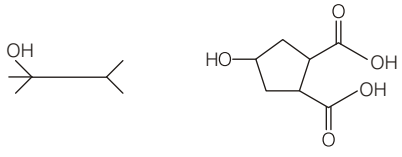
(a) 252 (b) 162
(c) 756 (d) 262

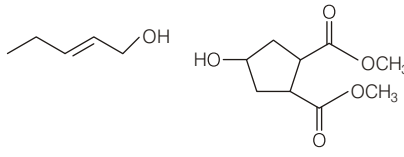
15. Identify the products of the following reactions.

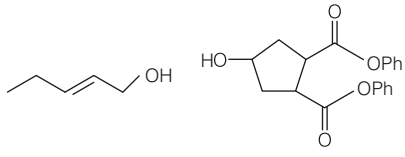
I. 

II. 

(a) 

(b) 

(c) 

(d) 

16. Which of the following statements are correct?

I. $SiCl_4$ and $SnCl_4$ behave like Lewis acids while CCl_4 does not.

II. Ge and Sn are oxidising agents while Pb is reducing agent.

III. CO_2 and PbO_2 both are acidic anhydrides.

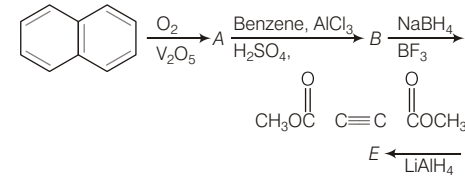
IV. $SnCl_2$ gives white precipitate with $HgCl_2$ which turns grey after some time while such reactions are not observed with $SnCl_4$.

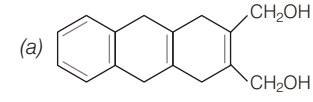
(a) I and IV (b) II and III
(c) I and II (d) I and III

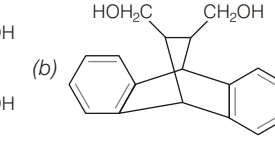
17. Dry air was drawn in succession through a series of vessels containing 3.2 g of substance. *X* in 72 g of C_2H_5OH and through similar set of vessels containing pure alcohol at the same constant temperature. The loss of weight in the first series of vessels was 2.2 g and in second series was 0.6 g. The molecular mass of *X* is

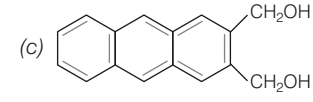
(a) 9.5 (b) 8.5
(c) 0.95 (d) 0.85

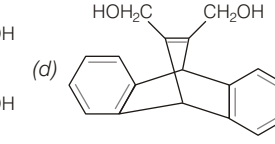
18. Identify the product *E* in the following reaction,



(a) 

(b) 

(c) 

(d) 

19. Which is the correct statement about the Ni¾N bond in $[Ni(NH_3)_6]^{2+}$?

(a) All are of equal bond lengths
(b) The four equatorial bonds are longer than the two axial bonds
(c) The two axial bonds are longer than the four equatorial bonds
(d) None of the bond length are equal

20. Identify the missing products of the following reactions:

I. $Na_2B_4O_7 \xrightarrow{760°C} \ldots A \ldots + B_2O_3$

II. $Si + KOH + H_2O \rightarrow \ldots B \ldots + H_2\uparrow$

III. $P_2O_5 + HNO_3 \rightarrow HPO_3 + \ldots C \ldots$

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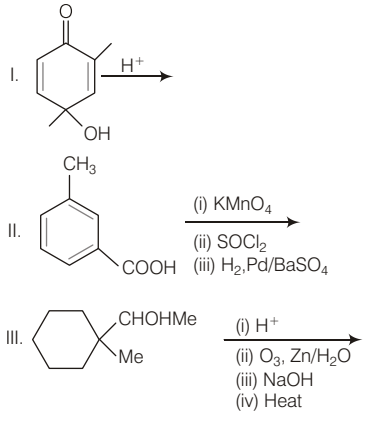
IV. $NH_3 + Cl_2$ (excess) $\rightarrow \ldots D \ldots + HCl$

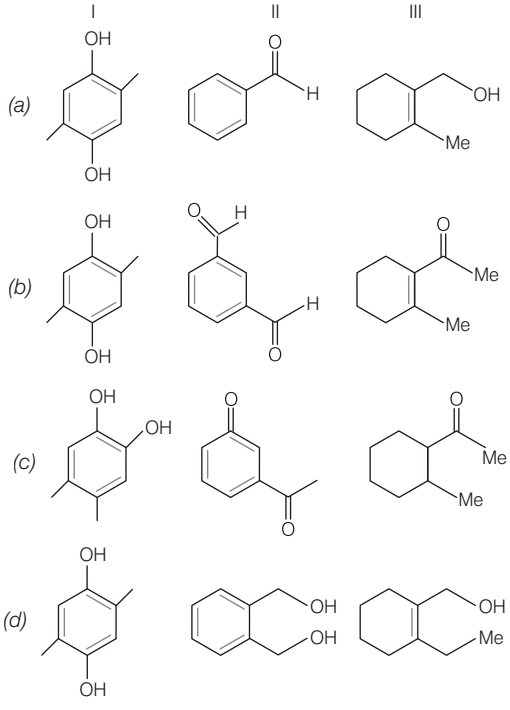
	A	B	C	D
(a)	Na_2O	$KSiO_3$	N_2O_4	NCl_3
(b)	$NaBO_2$	K_2SiO_3	N_2O_5	NCl_3
(c)	$NaBO_2$	K_2SiO_3	N_2O_4	$\overset{\oplus}{N}Cl_4$
(d)	Na_2O	K_2SiO_3	N_2O_5	NCl_3

21. At 298K, the specific conductivity of water is 6.21×10^{-8} ohm^{-1} cm^{-1}, the ionic conductance of $H^+$and $\overline{O}H$ ions at the same temperature are 438.2 and 212.6 ohm^{-1} cm^2 mol^{-1} respectively. The value of ionisation constant of water is

(a) 1.21×10^{-7} (b) 11.2×10^{-14}
(c) 1.21×10^{-14} (d) 2.2×10^{-14}

22. Identify the major product of the following reaction.





23. Which of the following statements are incorrect?

I. Hydrated $FeCl_3$ forms anhy. $FeCl_3$, on heating.
II. Solution of Hg_2Cl_2 turns black, when NH_3 is added in it.
III. Aqueous solutions of $HgCl_2$ and $SnCl_2$ can co-exist.
IV. CuCl is soluble in water while $CuCl_2$ insoluble.

(a) I, III and IV (b) II and III
(c) I, II and IV (d) III and IV

24. The vapour pressure of water at 100° C is 760 mm. The latent heat of vaporisation of water in this range is 41.27 kJ/mol. What will be the vapour pressure at 96° C?

(a) 658 (b) 758
(c) 858 (d) 958

25. In the decomposition of acetaldehyde in gaseous phase, various values of $\log_{10} k$ were plotted against $1/T$ and a straight line with a slope of −7525 was obtained. Similarly, a slope of −6045 was obtained in case of decomposition of acetone dicarboxylic acid. The energies of activation in the cases were, (Given, $R = 3$ cal/mol K)

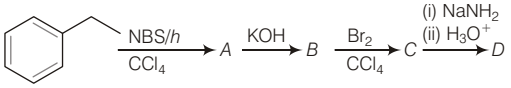
(a) 71, 990 and 41, 764 (b) 51,990 and 41,765
(c) 41, 764 and 51,990 (d) 61,990 and 51,764

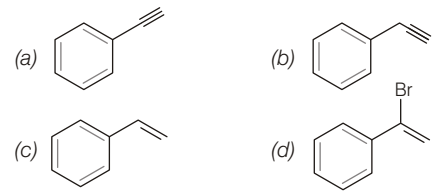
26. Which of the following statements are correct?

I. Ce (II) is more stable than Eu (II).
II. $La(OH)_3$ is more basic than $Lu(OH)_3$.
III. La^{3+} and Lu^{3+} are diamagnetic while other tripositive lanthanide ions are paramagnetic.
IV. Actinoids give oxocations.

(a) II, III and IV (b) I, II and IV
(c) II, III and IV (d) I, II and III

27. Identify the final product of the following reaction.





28. The octahedral complex of a metal ion M^{3+} with four monodentate ligands L_1, L_2, L_3 and L_4 absorb wavelengths in the region of red, green, yellow and blue, respectively. The increasing order of ligand strength of the four ligands is

(a) $L_4 < L_3 < L_2 < L_1$ (b) $L_1 < L_3 < L_2 < L_4$
(c) $L_3 < L_2 < L_4 < L_1$ (d) $L_1 < L_2 < L_4 < L_3$

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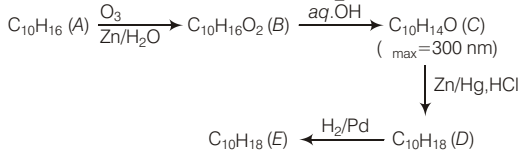
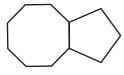
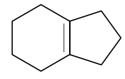
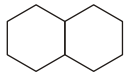
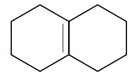
29. Give the structure for compound (*E*) in the following reaction.



(a) 

(b) 

(c) 

(d) 

30. Upon irradiation californium with neutrons, a scientist discovered a new nuclide having mass number of 350 and a half-life of 0.60 h. After four hours of the irradiation, the observed radioactivity due to the nuclide was 15 dis./min.

The atoms of the nuclide were prepared initially are

(a) 0.790×10^{-4}

(b) 0.790×10^{4}

(c) 7.79×10^{4}

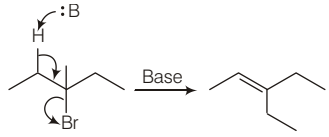
(d) 7.79×10^{-4}

Answer *with* Explanations

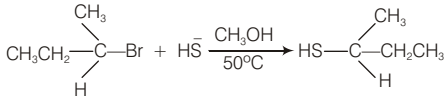
1. **(b)** A-q, B-p, C-s, D-r

A. $(CH_3CH_2)_3C\text{–}Br \xrightarrow[25^\circ C]{CH_3OH} (CH_3CH_2)_3C\text{–}OCH_3$

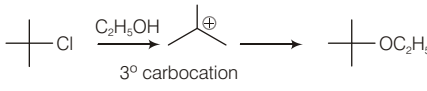
Since, $(CH_3CH_2)_3C$–Br forms very stable 3° carbocation and follows first order kinetics. In this type of reaction poor nucleophile is used.

B. 

Here, Br^- act as good leaving group, so at high temperature and in the presence of strong base elimination reaction takes place, i.e. reaction occurs at H followed by leaving of Br^-.

C. 

Due to the presence of strong nucleophile HS^- and formation of less stable and less crowded 2° carbocation substitution reaction takes place. Here rate of reaction depends upon both reactant and nucleophile. So, this reaction followed by second order reaction.

D. 

Formation of more stable 3° carbocation, reaction proceed at low temperature and follows S_N1 mechanism.

2. **(c)** If C_6H_6 had three isolated C = C double bonds, ΔH of hydrogenation of benzene would be close to three times of ΔH of hydrogenation of C_2H_4, i.e. – 98.1 kcal. The fact that enthalpy of hydrogenation of benzene is –49.2 kcal that benzene has been stabilised by resonance to the extent of 48.9 kcal / mol or 205 kJ/mol.

Hence, resonance energy = 98.1 – 49.2 = 48.9 kcal

3. **(b)** A→s-z. B→ r-x, C→ q-y, D→ p-w

4. **(c)** $Cu + Zn^{2+} \rightarrow Zn + Cu^{2+}$

$$E = E^\circ - \left(\frac{0.0592}{2}\right)\log\frac{[Cu^{2+}]}{[Zn^{2+}]}$$

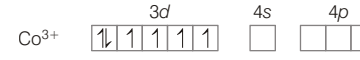
$$\therefore \quad 0 = (-1.10) - (0.0296)\log\frac{[Cu^{2+}]}{1.00}$$

$$\therefore \quad \log[Cu^{2+}] = \frac{-1.10}{0.0296} = -37.2$$

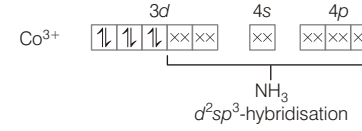
$$\therefore \quad [Cu^{2+}] = 6.31 \times 10^{-38}\ M$$

5. **(a)** Vitamins may remain stored except vitamin-C and some vitamins of B fight with the diseases.

6. **(d)** I. $[Co(NH_3)_6]^{3+}$, Co^{3+} ∴ d^6

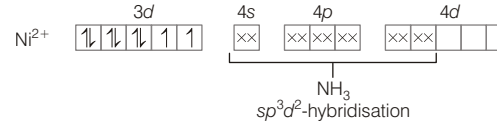


Due to the presence of NH_3 as strong field ligand, it pair up the electrons of metal ion and form inner orbital complex.

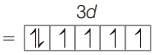


$[Ni(NH_3)_6]^{2+}$ Ni^{2+} d^8 =

There is no empty *d*-orbitals, so it cannot form inner orbital complex. In it, there is sp^3d^2 hybridisation and it forms outer orbital complex.



II. $[Fe(H_2O)_6]^{2+}$, weak field ligand present so, no pairing occurs.

Fe^{2+} ∴ d^6 = 

; $n = 4$

$\mu_{spin\ only} = \sqrt{n(n+2)}\ BM = \sqrt{4(4+2)} = \sqrt{24} = 4.89\ BM$

$[Fe(CN)_6]^{2+}$, strong field ligand present so, pairing will occur.

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Fe^{2+} ⇒ d^6 = ↿⇂ ↿⇂ ↿⇂ ☐ ☐ (3d) $n = 0$ $[\because \mu_{spin\ only} = 0]$

III. $[Fe(CN)_6]^{3-}$

Fe^{3+} ⇒ d^5 = ↿⇂ ↿⇂ 1 ☐ ☐ (3d)

One *d*-orbital is singly occupied, hence it is weakly paramagnetic in nature.

$[Fe(CN)_6]^{4-}$,

Fe^{2+} ⇒ d^6 = ↿⇂ ↿⇂ ↿⇂ ☐ ☐ (3d)

All orbitals are doubly occupied, hence it is diamagnetic in nature.

IV. $[NiCl_4]^{2-}$,

Ni^{2+} ⇒ d^8 = ↿⇂ ↿⇂ ↿⇂ 1 1 (3d) ☐ (4s) ☐ ☐ ☐ (4p)

Two unpaired electrons are present and Cl^- is weak field ligand so, no vacant 3*d*-orbital present.

Ni^{2+} in $[NiCl_4]^{2-}$ = ↿⇂ ↿⇂ ↿⇂ 1 1 (3d) ×× (4s) ×× ×× ×× (4p)

sp^3-hybridisation
Tetrahedral
Paramagnetic

In $[Ni(CO)_4]$

Ni^0 d^{10} = ↿⇂ ↿⇂ ↿⇂ ↿⇂ ↿⇂ (3d) ☐ (4s) ☐ ☐ ☐ (4p)

Ni^0 in $[Ni(CO)_4]$ = ↿⇂ ↿⇂ ↿⇂ ↿⇂ ↿⇂ (3d) ×× (4s) ×× ×× ×× (4p)

- sp^3-hybridisation
- Tetrahedral
- Diamagnetic

7. ***(c)*** In IV, ¾ NO_2 group at *para*-position in phenol exerts more electron withdrawing effect due to ¾ *R* and ¾ *I*-effects. In III, ¾ NO_2 group at *meta*-position exerts only-*I*-effect. Hence, III is more basic than IV due to more availability of lone pair of electrons on oxygen atom. In I and II, II is more basic than I because in II methyl group exerts electron donating effect due to which electron density on oxygen atom increases.

8. ***(b)*** $HCOOH + H_2O \rightleftharpoons HCOO^- + H_3O^+$

$$K_a = \frac{[HCOO^-][H_3O^+]}{[HCOOH]} = 1.80 \times 10^{-4}$$

I. $$K_a = \frac{(0.060 + x)x}{0.050 - x} = 1.80 \times 10^{-4}$$

⇒ $x = 1.46 \times 10^{-4}$

⇒ pH = 3.84

II. $$K_a = \frac{(0.0060 + x)x}{0.0050 - x} = 1.80 \times 10^{-4}$$

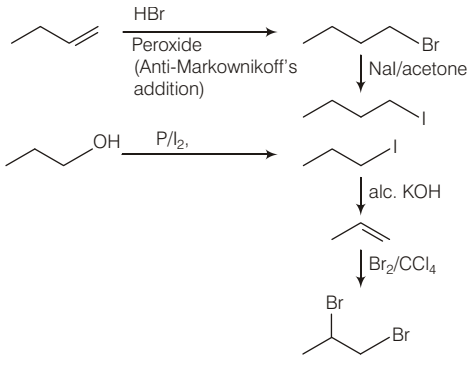
⇒ $x = 1.45 \times 10^{-4}$

⇒ pH = 3.84

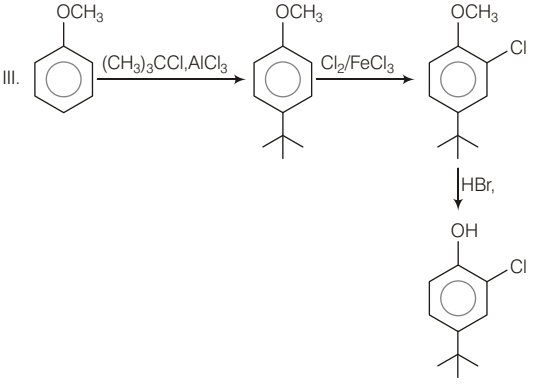
III. $$K_a = \frac{(0.00060 + x)x}{0.00050 - x} = 1.80 \times 10^{-4}$$

⇒ $x = 1.02 \times 10^{-4}$

⇒ pH = 3.99

9. ***(b)*** I. 

II.

III. 

10. ***(d)*** I. Zn is stronger reducing agent than Cu and cheaper than Cu also.

$$Zn + 2[Ag(CN)_2]^- \rightarrow [Zn(CN)_4]^- + 2Ag$$

II. Due to the formation of blue copper tetramine sulphate, $[Cu(NH_3)_4]SO_4$ complex.

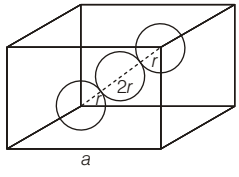
III. When brought in contact of skin, it leans black stain as present on moon.

IV. NaCl is ionic compound and Cl^- ions obtained form it react with Ag^+ to form white $AgCl.CCl_4$ is covalent compound so it does not give Cl^- and white precipitate of AgCl.

11. ***(b)*** For body-centred cubic,

Body diagonal = $4r = \sqrt{3}a$

$$\therefore \quad a = \frac{4r}{\sqrt{3}}$$



Number of atoms per unit cell

$$(Z) = \frac{1}{8} \times 8 + 1 = 2$$

For face-centred cubic,

Face diagonal = $4r = \sqrt{2}a$

$$\therefore \quad a = 2\sqrt{2}r$$

Number of atoms per unit cell $(Z) = \frac{1}{8} \times 8 + 6 \times \frac{1}{2} = 4$

$$\text{Density} = \frac{ZM}{N_0 \times a^3}$$

$$\therefore \text{ Density ratio} = \frac{\gamma}{\alpha} = \frac{\frac{4}{(2\sqrt{2}r)^3}}{\frac{2}{(4r/\sqrt{3})^3}} = \frac{4/(2^{9/2})}{2/(4^3/3^{3/2})} = \frac{4\sqrt{2}}{3\sqrt{3}} = 1.09$$

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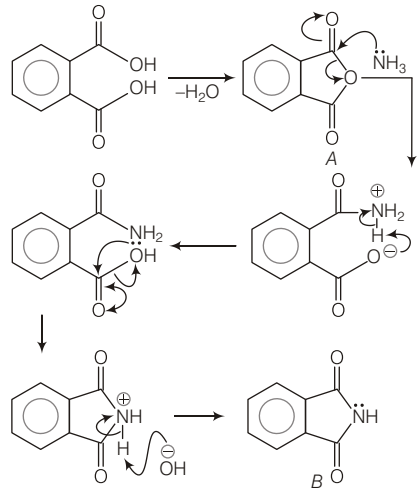
12. **(b)**



13. **(c)** On moving from VO_4^{3-} to CrO_4^{2-} to MnO_4^- the charge on metal increases as $V^{5+} < Cr^{6+} < Mn^{7+}$.

V^{5+}, Cr^{6+} and Mn^{7+} have vacant *d*-orbitals, so electrons from 2*p* orbitals of O^{2-} get excited to 3*d*° orbitals of metal. Hence, charge transfer occurs from ligand to metal.

Since, size of metal cations decreases in the order $V^{5+} > Cr^{6+} > Mn^{7+}$ therefore, energy of charge transfer decreases in the following order:

$$VO_4^{3-} > CrO_4^{2-} > MnO_4^-$$

Energy ←

Wavelength →

14. **(c)** Volume of dry air at STP

$$= 62.5\ L\left(\frac{273}{296}K\right)\left[\frac{740-27.5}{760}\text{torr}\right] = 54\ L$$

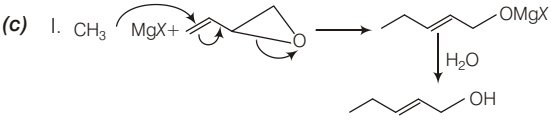
Rate of oxygen consumption

$$= \frac{\text{Volume of oxygen (STP) consumed}}{\text{Time in which this volume was consumed}}$$

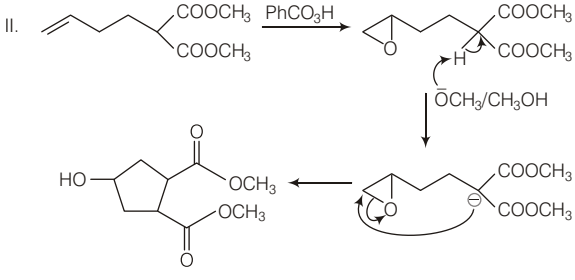
$$= \frac{(0.2545 - 0.1564) \times 54\ L}{7\ \text{min}}$$

$$= 0.756\ L/\text{min} = 756\ mL/\text{min}$$

15. **(c)** I.



II.



16. **(a)** I. Due to the presence of vacant *d*-orbitals in Si and Sn, they have ability to accept lone pair of electrons and are easily hydrolysed. But in case of CCl_4, C has no vacant *d*-orbital so, it does not act as Lewis acid.

II. Pb is metal so it has high oxidation potential. Sn and Ge have high reduction potential because Sn is metalloid and Ge is non-metal. Hence, they have higher tendency to accept electrons. So they behave as a reducing agent while Pb behaves as an oxidising agent.

III. Carbon is non-metal and its oxide is acidic in nature while Pb is metal and its oxide is basic in nature.

IV. $SnCl_2$ is strong reducing agent and it reduces Hg^{2+} to Hg_2^+ and further Hg_2^+ reduced to Hg which is ash coloured. While $SnCl_4$ does not act as a reducing agent.

17. **(a)** Loss in weight of solution $\mu\ p_s = 2.2$ g

Loss in weight of alcohol $\mu\ p - p_s = 0.6$ g

Total loss $\mu\ [p_s + (p - p_s)] = 2.2 + 0.6 = 2.8$ g

Suppose *m* be the molar mass of *A*

Molar mass of alcohol, $M = 46$ g

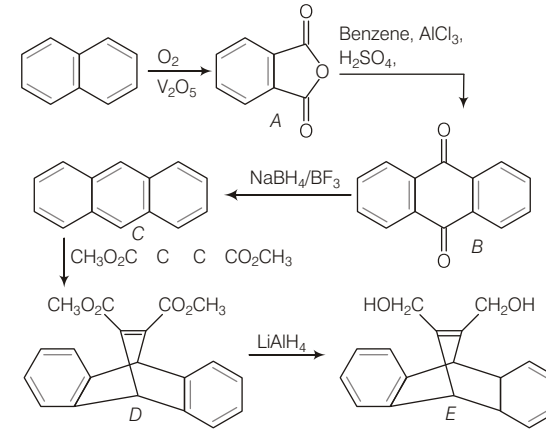
Weight of substance *X*,

$$w = 3.2\ g$$

$$\therefore \quad \frac{p - p_s}{p} = \frac{wM}{mW} \quad \Rightarrow \quad \frac{0.6}{2.8} = \frac{3.2 \times 46}{m \times 72}$$

$$\therefore \quad m = \frac{2.8 \times 3.2 \times 46}{0.6 \times 72} = 9.5$$

18. **(d)**



19. **(a)** In complex $[Ni(NH_3)_6]^{2+}$, the splitting is small because charge on metal cation is not high and the ligands are also not too strong. Therefore, these complexes are considered to be regular octahedral and the energy of d_{z^2} and $d_{x^2-y^2}$ will be same, i.e. e_g orbitals are degenerate and thus all Ni–N bonds are equal.

20. **(b)**

$$Na_2B_4O_7 \xrightarrow{760°C} \underset{A}{2NaBO_2} + B_2O_3$$

$$Si + 2KOH + H_2O \rightarrow \underset{B}{K_2SiO_3} + 2H_2\uparrow$$

$$P_2O_5 + 2HNO_3 \rightarrow 2HPO_3 + \underset{C}{N_2O_5}$$

$$NH_3 + 3Cl_2(\text{excess}) \rightarrow \underset{D}{NCl_3} + 3HCl$$

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21. **(c)** $\Lambda_C = \frac{1000 \times \kappa}{C} = \frac{1000 \times 6.21 \times 10^{-8}}{C}$,

$\Lambda_\infty = \Lambda_{H^+} + \Lambda_{OH^-} = 438.2 + 212.6 = 550.8 \text{ ohm}^{-1}\text{cm}^2\text{mol}^{-1}$

Water may be considered to be the dilute solution of H^+ and OH^- ions in dissociated molecule of H_2O. Therefore, Λ_c will be taken as Λ_∞.

$\therefore \quad 550.8 = \frac{1000 \times 6.21 \times 10^{-8}}{C}$

$\Rightarrow \quad C = \frac{1000 \times 6.21 \times 10^{-8}}{550.8}$

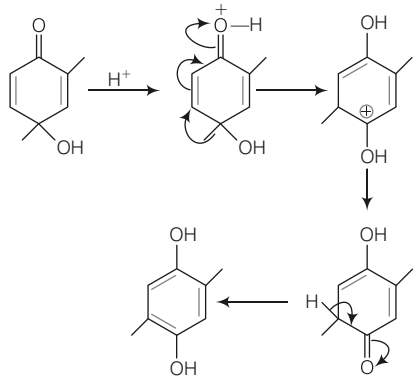
$= 1.1 \times 10^{-7} \text{ mol/cm}^3$

$K_w = [H^+][OH^-]$

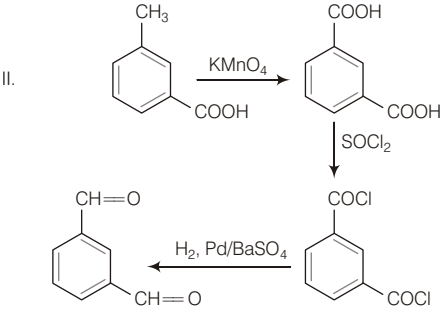
$= 1.1 \times 10^{-7} \times 1.1 \times 10^{-7}$

$= 1.21 \times 10^{-14}$

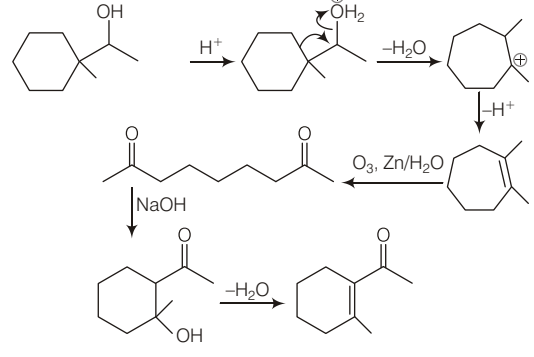
22. **(b)** I.



II.



III.



23. **(a)** I. Hydrated $FeCl_3$ does not form anhyd. $FeCl_3$, on heating because it forms Fe_2O_3.

$$2FeCl_3 \times 6H_2O \xrightarrow{\Delta} Fe_2O_3 + 6HCl + 9H_2O$$

II. Solution of Hg_2Cl_2 turns black, when NH_3 is added in it this is due to formation of $HgNH_2Cl$ (black).

III. Aqueous solution of $HgCl_2$ and $SnCl_2$ cannot co-exist because $SnCl_2$ reduces $HgCl_2$ to Hg.

IV. CuCl is insoluble in water while $CuCl_2$ is soluble because according to Fajans' rule CuCl is preferably covalent in nature.

24. **(a)** From Clapeyeron-Clausius equation,

$$\log \frac{p_2}{p_1} = \frac{\Delta H_V}{2.303\, R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

Given that,

$p_1 = 760$ mm, $T_1 = 100°$ C $= 373$ K

$p_2 = ?$, $T_2 = 96°$ C $= 369$ K

From above equation,

$$\log \frac{p_2}{760} = \frac{41270}{2.303 \times 8.314}\left[\frac{369 - 373}{369 \times 373}\right]$$

$$\log p_2 - \log 760 = \frac{41270 \times (-4)}{8.314 \times 2.303 \times 369 \times 373}$$

$= -0.0626$

$\Rightarrow \quad \log p_2 - 2.8808 = -0.0626$

$\Rightarrow \quad \log p_2 = -0.0626 + 2.8808$

$= 2.818$

$\therefore \quad p_2 = 658$ mm.

25. **(b)** From Arrhenius equation we know that

$$\text{Slope} = -\frac{E_a}{2.303 \times R}$$

$$= -\frac{E_a}{2.303 \times 3}$$

For the decomposition of acetaldehyde

$$-7525 = -\frac{E_a}{6.909}$$

$\therefore \; E_a = 51{,}990$ cal/mol

Similarly, for the decomposition of acetone dicarboxylic acid.

$$-6045 = -\frac{E_a}{6.909}$$

$\therefore \; E_a = 41{,}765$ cal/mol

26. **(a)** I. Ce(II) is less stable than Eu(II)

Ce(II) = [Xe] $4f^1 5d^1$; Eu(II) = [Xe] $4f^7 5d^0$

Due to half-filled *f*-orbitals in Eu(II), it is more stable than Ce(II)

II. Lu^{3+} is smaller than La^{3+} so $Lu(OH)_3$ is more covalent than $La(OH)_3$ according to Fajans' rule. So, $La(OH)_3$ is more basic than $Lu(OH)_3$.

III. La^{3+} has $4f^0$ and Lu^{3+} has $4f^{14}$ configuration so, they are diamagnetic but other tripositive ions are paramagnetic.

IV. Actinoid gives oxocations, e.g. UO_2^{2+}.

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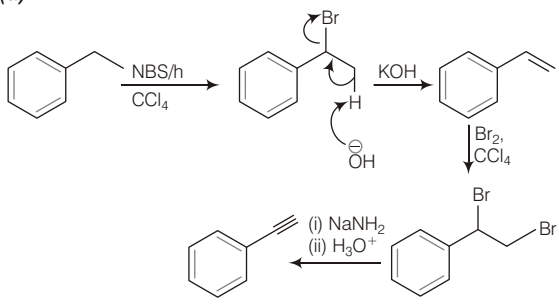
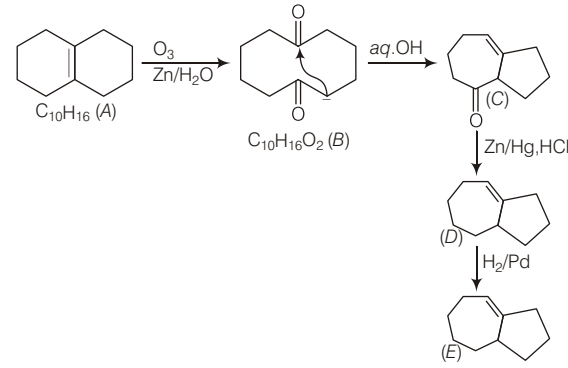
27. **(a)**





28. **(b)** Ligand field strength μ energy of light absorbed

$\mu \frac{1}{\text{wavelength of light absorbed}}$

Energy order for these region is,

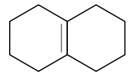
Blue (L_4) < green (L_2) > yellow (L_3) > red (L_1)

∴ Ligand strength order is, $L_4 > L_2 > L_3 > L_1$.

29. **(a)** Double bond equivalent (DBE)

$$= C_n - \frac{H_n}{2} + 1 = 10 - \frac{16}{2} + 1 = 3$$

(May be two rings and one double bond)

$C_{10}H_{16}$ ≡ 

30. **(c)** At $t_0 = 0, r_0 = \lambda \times N_0$

At $t = 4\text{h}, r_1 = \lambda \times N$

$$\therefore \quad 15 = \frac{0.693}{0.60 \times 60} \times N \qquad \left(\because \lambda = \frac{0.693}{t_{1/2}}\right)$$

$$\therefore \quad N = 799.22$$

From $2.303 \log \frac{N_0}{N_1} = \lambda t$

At $t = 4$ h, $\frac{0.693 \times 4 \times 60}{0.60 \times 60} = 2.303 \log \frac{N_0}{779.22}$

$$\Rightarrow \quad 4.62 = 2.303 \log \frac{N_0}{779.22}$$

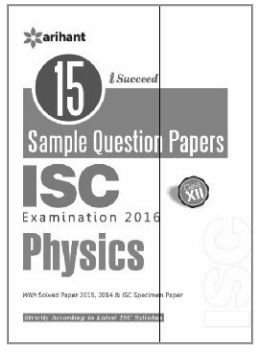
$N_0 = 7.79 \times 10^4$ atoms

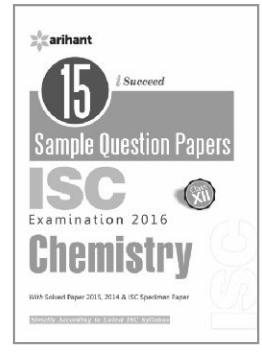
i Succeed

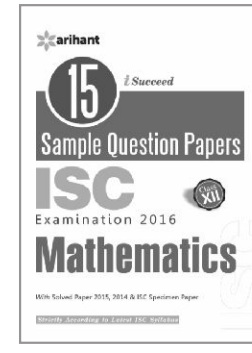
SAMPLE QUESTION PAPERS

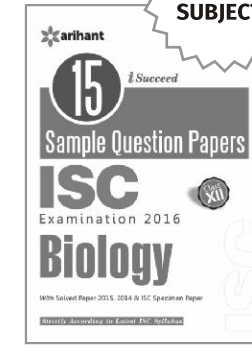
for **ISC Class XII**

AVAILABLE IN ALL SUBJECTS









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DO YOU KNOW?

- **Do you know, we have the digital atomic photograph of all the atoms except those of H and He.**

  The scanning tunneling microscope (STM) is an exciting analytical instrument that provides images of individual atoms or molecules on a surface of metal. To do this, a metal probe in the shape of a needle with an extremely fine point is brought extremely close to the sample surface being examined. The voltage is then applied between the probe and the sample surface, when the tip is close enough to the sample, electrons jump between the probe and the sample in a process called tunneling. Current is used-*via* a feedback loop to maintain a constant vertical distance from probe tip to sample.

  The resulting movements are captured by a computer that records the surface height at each location on the surface. The STM image, which appears much like a photographic image, shows the locations of atoms on the surface being investigated.

- **Do you know that the quarks inside a proton can change colour although overall colour of proton will remains same.**

  Quarks inside of a proton can change colour by exchanging gluons, the virtual particles that carry the strong force and hold quarks together. But the overall colour of the proton remains white, because the three valence quarks in a proton are always red, green and blue. So, when one quark changes its colour, another quark also changes its colour as well.

- **What is the relevance of empty space of atoms in our body?**

  The atoms that make up our body are mostly empty space, so despite there being so many of them, without that space we would compress into a tiny volume. The nucleus that make up the vast bulk of the matter in an atom is so much smaller that the whole structure is comparable to the size of a pea in the centre of football stadium. If we lost all our empty space, our body would fit into a cube less than $\frac{1}{500}$th of centimetre on each side.

- **Do you know that line spectrum is sometimes referred to as an "atomic fingerprint".**

  Emission spectra revealed that each element produced a unique set of spectral lines. This observation indicates that the energy levels must be unique for atoms of each element.

  Therefore, a line spectrum is sometimes referred to as an "atomic fingerprint".

  Atomic fingerprints are useful in the identification of elements. For instance, in 1868 the atomic fingerprint of a new element was observed in the spectrum from the Sun. This element was named as helium, after helios, the Greek word for "Sun." In 1895, an element was discovered in uranium ore with an atomic fingerprint identical to that observed for helium in the Sun's spectrum. Thus, helium was discovered on Earth after 27 years it had been first observed in the solar spectrum.

- **Do you know, electron, proton and neutron also have their own subparticles.**

  Although electron, proton and neutron were considered as fundamental particles of atom but now proton and neutron are known to be composed of three valence quarks (elementary particles of matter) classified as baryons. Protons are composed of two up quarks (each with charge $\frac{2}{3}$) and one down quark (with charge $\frac{1}{3}$ while neutrons consist one up quarks $\frac{1}{3}$ and two down quarks $\frac{2}{3}$. However, electrons are truely elementry particles with no internal structures. Electron is a type of lepton (an elementry, half-integer spin particle that does not undergo strong interaction). There are six types of lepton out of which electron has the least mass. The heaviour leptons are mostly unstable and change rapidly into electrons through process of particle decay.

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Reaction 1

(i) Reduction of alcohols, acids and acid derivatives is carried out by heating them with red phosphorus and HI but in this process yield of alkanes are very less.

(ii) For reduction of aldehydes and ketones into alkanes following reagents are used :
- Red P + HI / Δ
- Zn - Hg / conc. HCl (Clemmensen reduction)
- Hydrazine followed by C_2H_5ONa at 180 °C (Wolff-Kishner reduction)

(iii) The generalised reducing agents used can be metal + proton donor acids and complex hydrides such as Sn / HCl, Zn / CH_3COOH, Zn—Cu couple with CH_3OH, Na with ethanol etc.
- Among the complex hydrides lithium aluminium hydride (LAH) is the best reagent and other includes $NaBH_4$, $NaAlH_4$, Ph_3SnH etc. LAH is a strong reducing agent because it reduces four molecules at a time.

The latter on acid hydrolysis with HCl yield 4 molecules of $>C<^{OH}_{H}$ along with $AlCl_3$ and LiCl.

(iv) Primary and secondary alkyl halides give alkanes on reaction with $LiAlH_4$, while tertiary alkyl halides give mainly alkenes.

(v) Alkenes on reduction with $B_2H_6(BH_3)$ in the presence of Lewis bases like tetrahydrofuran (THF), diethylene glycol methyl ether (DIGLYME) which convert dimeric B_2H_6 to BH_3 by forming acid base complex followed by the treatment of protic agent ($AgNO_3$ / NaOH) forms alkanes having longer carbon chains.

$AgNO_3$ / NaOH is called **coupling reagent** and this reaction is called **coupling reaction** or hydroboration reaction.

Note Coupling reaction seems to follow anti Markownikoff addition. But it is Markownikoff's addition in reality. The difference here only in BH_3, the H plays the role of negative partner while boron plays the role of positive partner.

Reaction 2 Hydrogenation or catalytic reduction
The best catalyst is used for this reaction is Raney Ni.
- Raney Ni is more effective over normal Ni (works at 200 – 300 °C) as it can work even at room temperature.
- Other catalysts besides Ni are Pd, Pt etc., these also require a temperature between 200 – 300 °C.
- The reduction of unsaturated hydrocarbons with Ni at temperature between 200 – 300 °C is called **Sabatier Sanderens reaction**.

Reaction 3
- Decarboxylation elimination of CO_2 from a carboxylic acid is called decarboxylation. Hot soda lime (NaOH / CaO) is frequently used reagent for this reaction.
- In this reaction, produced alkanes contain one less carbon atom than the original acid.

Reaction 4 This is good method to prepare hydrocarbons (alkanes) having odd number of carbon atoms.

Reaction 5 Grignard reagent (*R*Mg*X*) on treatment with compounds like H_2O, ROH, acids etc., forms alkanes.

Reaction 6 This method is used to create a new C—C linkage and used to prepare alkanes and alkynes as well.

Note
- CH_4 cannot be prepared by this method.
- This method is not suitable for alkanes having odd number of carbon atoms, as in such cases a mixture of hydrocarbons is formed which is difficult to separate.

Reaction 7
- For single type of alkyl halide, a single product is obtained.
- For different alkyl halides, mixture of alkanes are obtained.

Note CH_4 cannot be prepared by this reaction.

Reaction 8 In this method, Zn is used in place of Na. Here, rest of the things remain absolutely same as in the Wurtz reaction.

SOME OTHER METHODS TO PREPARE ALKANES

(a) **From Carbides** CH_4 is prepared by treated carbides (Al_4C_3 and Be_2C) with water.

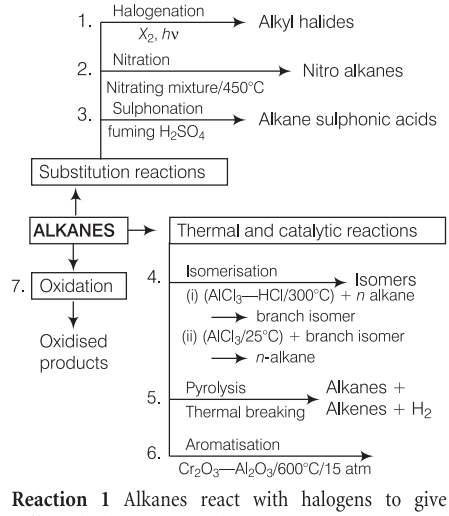
(b) **From Constituents** Lower alkanes are prepared by this method in which build upto a chemical compound is done by its constituent elements as :

$$C + 2H_2 \xrightarrow[1473K]{\text{Electric arc}} CH_4$$

PHYSICAL PROPERTIES OF ALKANES

- First four alkanes are gases, next 13 are colourless liquids and all other higher alkanes are waxy solids.
- Insoluble in water but soluble in alcohol, ether, benzene etc. The solubility diminishing with increase in molecular weight.
- As the number of carbon atoms increases, the boiling points of alkanes increase. However, branching result in decrease in boiling point due to decreased surface area.
- Dipole moment of all alkanes is zero.
- Melting point of alkanes increases with increase in molecular weight but alkanes with even number of carbon atoms have higher melting point than the preceeding and succeeding members.

CHEMICAL PROPERTIES OF ALKANES



Reaction 1 Alkanes react with halogens to give different halogenated products.

e.g. $CH_4 + Cl_2 \xrightarrow[-HCl]{h\nu \text{ or } 473-523K} CH_3Cl + CH_2Cl_2 + CHCl_3 + CCl_4$

- Halogens react in the order, $I_2 < Br_2 < Cl_2 < F_2$.

Revisi CONCEI HYDROCARB

Hydrocarbons are chemical compounds consisting entirely ca bonds.

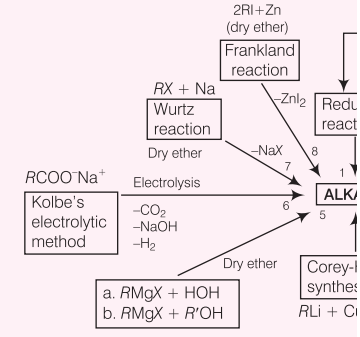
CLASSIFICATION OF HYDROCARBONS

These are classified into two categories : (A) Alipha

Aliphatic Hydrocarbons (a) Alkanes (Paraffins) C_nH_{2n+2}. T

METHODS OF PREPARATION

The methods of preparation are summarised in the following



- Those compounds which have atleast one hydrogen atom present on sp^3 hybrid C-atom, give halogenation reaction.
- Reactivity order of sp^3 hybrid C-atom is as follows :

tert-benzyl carbon > 2 °-benzyl carbon > *p*-benzyl carbon > 3 °-allylic carbon > 2 °-allylic carbon > *p*-allylic carbon > 3 °-alkyl carbon > 2 °-alkyl carbon > *p*-alkyl carbon > CH_4.

Reaction 2 Higher alkanes (having more than 5 carbon atoms) can be nitrated, when heated with fuming HNO_3. This reaction is called liquid phase nitration.

Reaction 3 Sulphonation is normally given by alkanes with minimum 6 C-atoms onwards.

Reaction 4 Isomerisation is a result of molecular rearrangement involving 1, 2-hydride or methyl shift. Anhyd. $AlCl_3$ is used as a reagent for this reaction.

Reaction 5 Pyrolysis is breaking of organic molecules and when the process is applied to higher alkanes, it is called cracking.

Reaction 6 It is applicable to alkanes from hexane to decane.

Reaction 7
- Oxidation can be complete or partial. Complete oxidation is called *combustion.*
- When alkanes are burnt in insufficient supply of oxygen, CO and carbon black are obtained.
- Alkanes having 3° hydrogen are oxidised by $KMnO_4$ and $K_2Cr_2O_7$ and give corresponding alcohols. Lower alkanes undergo restricted oxidation in the presence of metallic catalysts such as Cu at high temperature and pressure to form alcohols, aldehydes, ketones and acids.

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on through PT MAP

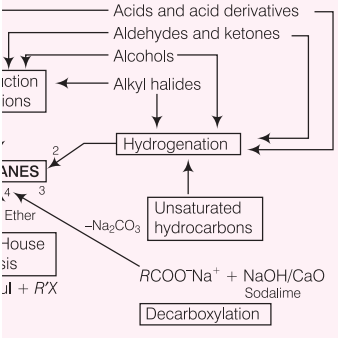
ONS (PART I)

bon and hydrogen atoms bonded to each other by covalent

ic (B) Aromatic

he main source of alkanes are natural gas and petrolium.

chart :



- Methane or ethane with oxygen at high pressure and comparatively low temperature are oxidised and give H_2O and CO_2.

(b) ALKENES (OLEFINS) C_2H_{2n}

Their main source is petroleum.

Method of Preparation of Alkenes

Reaction 1 Alkyl halides when treated with alc. KOH / Δ give alkenes. Ease of dehydrohalogenation is 3° > 2° > 1° for alkyl halides.

Reaction 2 Alcohols when treated with conc. H_2SO_4 at 170° C, give alkenes. Ease of dehydration is 3° > 2° > 1°.

Reaction 3 *Vicinal* dihalides give alkenes while *geminal* dihalides gives alkynes. When heated with Zn dust.

Reaction 4 Alkynes on hydrogenation with Lindlar's catalyst or nickel boride (P-2 catalyst) or with Na or Li in liquid ammonia, give alkenes. However in case of Lindlar's catalyst, *cis* alkene is obtained while in case of Na or Li in liq. NH_3 (Brich reduction) *trans* alkene is obtained.

Reaction 5 On hydroboration of alkynes and alkenes are obtained.

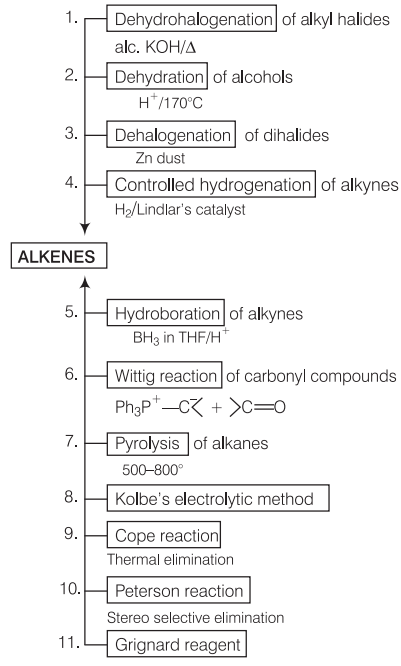
Reaction 6 In Wittig reaction there is nucleophilic addition of triphenyl phosphonium (ylide) ion which result to alkene.

Reaction 8 On electrolysis of sodium or potassium salt of dicarboxylic acid, we get alkenes.

Reaction 9 When a 3° amine oxide containing atleast one β-hydrogen is heated at 150° C, it decomposes to form an alkene and a derivative of hydroxyl amine.

Reaction 10 β-hydroxy alkyl silane elimination reaction in the presence of acid as well as base.

METHOD OF PREPARATION OF ALKENES



Reaction 11 When Grignard reagent is treated with vinyl halide, alkenes are obtained.

PHYSICAL PROPERTIES OF ALKENES

- First three alkenes are gases, next 14 are liquids and rest are solids.
- All alkenes are colourless and odourless except ethene which has pleasent odour.
- Boiling point ∝ number of carbon atoms ∝ $\frac{1}{\text{Branching}}$.
- *Cis* alkene has more dipole moment and boiling point than corresponding *trans* alkene.

However, the melting point of *trans* alkene is more than the corresponding *cis*-alkene.

- The alkenes follow the following order of stability

$R_2C=CR_2 > R_2C=CHR > R_2C=CH_2 - RCH-CHR\,(trans > cis) > R-CH=CH_2 > CH_2=CH_2$

Reaction 2 This reaction is used in the test of unsaturation. When Br_2 is added as Br_2 water, the colour of Br_2 water disappears.

Reaction 3 The addition of haloacids is frequently carried out by passing dry gaseous haloacid in moderately polar solvent.

Reaction 4 The hypohalous acid breaks into $\overline{O}H$ and X^+ ions and X^+ ion attack on π-bond.

Reaction 5 The addition of H_2O takes place according to Markownikoff's rule.

Reaction 6 The process of alkylation occurs through intermolecular hydride shift from branched alkane.

Reaction 7 In case of OsO_4 *syn*-addition takes place while with peroxy acids *anti*-addition takes place.

Reaction 9 Alkene reacts with ozone and forms ozonide. After the addition of H_2O in the presence of Zn / CH_3COOH, carbonyl compounds are obtained.

Reaction 11 Dimerisation has the similarity with alkylation. In the absence of branched alkane and at high temperature, the carbonium ion formed eliminates H^+ resulting to alkene formation again.

Reaction 12 In this reaction conjugated diene attacked by olefin.

Reaction 13 Ethylene on reaction with sulphur monochloride forms mustard gas.

Reaction 14 In this reaction, the hydrogen atom present at allylic position is substituted by halogen atom.

Reaction 15 Polymerisation

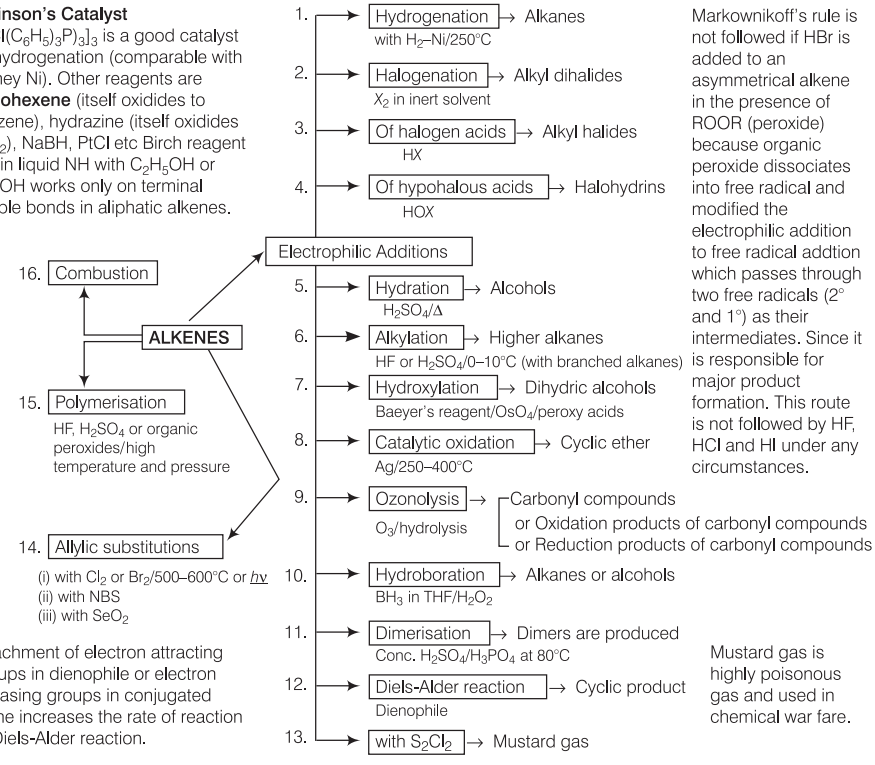
$$n\underset{\text{Ethene}}{CH_2=CH_2} \longrightarrow \underset{\text{Polythene}}{+CH_2-CH_2+_n}$$

Reaction 16

$$C_nH_{2n} + \frac{3n}{2}O_2 \longrightarrow nCO_2 + nH_2O + \text{Heat}$$

CHEMICAL PROPERTIES OF ALKENES

Willinson's Catalyst
$RhCl(C_6H_5)_3P)_3]_3$ is a good catalyst for hydrogenation (comparable with R aney Ni). Other reagents are **cyclohexene** (itself oxidides to benzene), hydrazine (itself oxidides to N_2), NaBH, PtCl etc Birch reagent (Na in liquid NH with C_2H_5OH or CH_3OH works only on terminal double bonds in aliphatic alkenes.



Markownikoff's rule is not followed if HBr is added to an asymmetrical alkene in the presence of ROOR (peroxide) because organic peroxide dissociates into free radical and modified the electrophilic addition to free radical addtion which passes through two free radicals (2° and 1°) as their intermediates. Since it is responsible for major product formation. This route is not followed by HF, HCl and HI under any circumstances.

Attachment of electron attracting groups in dienophile or electron releasing groups in conjugated diene increases the rate of reaction of Diels-Alder reaction.

Mustard gas is highly poisonous gas and used in chemical war fare.

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Questions to Measure Your Problem Solving Skills

1. Fill in the blanks. Choose the correct option.

I. It would take …*A*… years to spend one Avogadro's number of rupees at a rate of 10 lakhs of rupees in one second.

II. The equivalent weight of a metal is double than that of oxygen. The weight of its oxide is …*B*… times greater than the weight of metal.

III. Specific heat of a metal is 0.056 and its chloride contains 49.5% chlorine. The atomic mass of the metal/element is …*C*… .

IV. The density of a solution containing 13% by mass of sulphuric acid is 1.09 g/mL. The molarity of solution is …*D*… .

	A	B	C	D
(a)	1.90×10^{10}	1.5	108.6	1.44 M
(b)	6.02×10^{10}	0.5	114.3	2.89 M
(c)	3.01×10^{10}	2.0	48.01	0.200 M
(d)	7.30×10^{10}	2.5	36.21	0.500 M

2. The rate of inversion of cane sugar to dextrose and laevulose by dilute acid is observed by measuring the polarisation angle at various times when the following results are obtained.

t (min)	Angle
0	32.4
10	28.8
20	25.5
30	22.4
40	19.6
100	−6.1
∞	−14.1

Calculate time (*t*) in min, when the solution is optically inactive.

(a) 86.6 min *(b)* 72.4 min
(c) 65 min *(d)* 91 min

3. Which of the following statements is/are correct? Choose the correct option.

I. Addition of high proportions of manganese makes steel useful in making rails of rail road because manganese gives hardness to steel and can remove oxygen and sulphur.

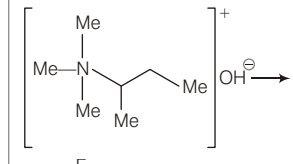
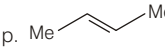
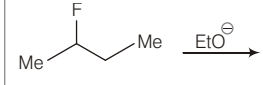
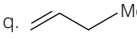
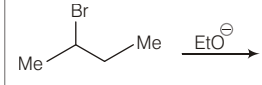
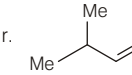
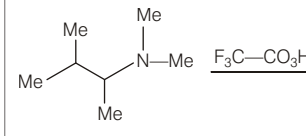
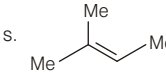
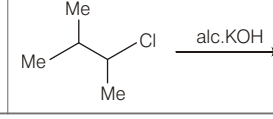
II. In the dichromate anion, 4Cr ¾ O bonds are equivalent.

III. Anhy. $FeCl_3$ is prepared by reaction of metallic iron with hydrochloric acid.

IV. Lanthanoid contraction is due to poor shielding of 4*f*-electrons by 5*d*-electrons.

(a) Only I *(b)* Only II *(c)* I and III *(d)* III and IV

4. Match the following (Column I) which represents reactions to the (Column II) representing their products.

	Column I	Column II
A.		p. 
B.		q. 
C.		r. 
D.		s. 
E.		

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Codes

	A	B	C	D	E
(a)	q	q	p	r	s
(b)	p	q	r	r	s
(c)	s	r	q	q	r
(d)	r	s	s	p	p

5. The values of $E°$ for some of the reactions are given below.

$$E°_{I_2/I^-} = +0.54\,V;\ E°_{Cl_2/Cl^-} = +1.36\,V$$

$$E°_{Fe^{3+}/Fe^{2+}} = +0.76\,V;\ E°_{Ce^{4+}/Ce^{3+}} = +1.60\,V$$

$$E°_{Sn^{4+}/Sn^{2+}} = +0.15\,V$$

On the basis of above data, state whether following statements are correct or incorrect?

I. Fe^{3+} oxidises Ce^{3+}.

II. I_2 displaces chlorine from KCl.

III. Reaction between $FeCl_3$ and $SnCl_2$ occurs.

Choose the correct statement.

(a) I and II (b) II and III (c) I and III (d) Only III

6. Fill in the blanks. Choose the correct option.

I. ...*A*... ligand is capable of forming low spin as well as high spin complex.

II. $[Co(NO_2)_6]^{3-}$ is ...*B*... spin complex.

III. $[CoCl_6]^{3-}$ is ...C... spin complex.

IV. $Fe_2(CO)_9$ is diamagnetic due to ...*D*... .

	A	B	C	D
(a)	CO	low	high	presence of one CO as bridge group
(b)	CN^-	high	low	presence of monodentate ligand
(c)	NH_3	low	high	Fe—Fe bond in molecule
(d)	NO_2^-	high	low	Resonance hybridisation of CO

7. Which of the following statements is/are incorrect? Choose the correct option.

I. Cross-linked silicon polymer is obtained on hydrolysis of $RSiCl_3$.

II. When phosphine gas is mixed with chlorine gas, $PH_3 \times Cl_2$ is formed on warming up.

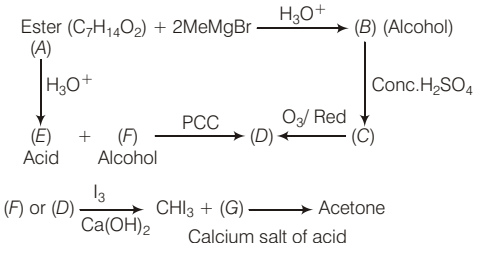
III. The oxidation state of sulphur is never less than + 4 in its compounds.

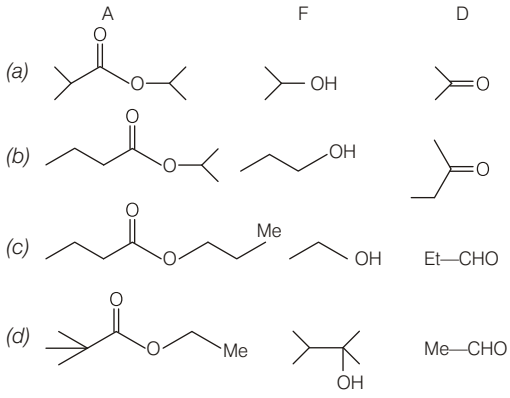
IV. Increasing order of strength of oxo-acids of chlorine is $HClO > HClO_2 > HClO_3 > HClO_4$

V. XeF_6 on complete hydrolysis gives Xe.

(a) Only I (b) II and III (c) IV and V (d) II, III, IV and V

8. Complete the following sequence of reaction and choose the correct option.





9. During the discharge of a lead storage battery, density of H_2SO_4 fell from 1.294 to 1.139 g/mL. Sulphuric acid of density 1.294g/mL is 39% H_2SO_4 by weight and that of density 1.139 g/mL is 20% H_2SO_4 by weight. The battery holds 3.5 L of the acid and volume remains practically constant during discharge. Calculate ampere-hour of which the battery must have been used.

(a) 452.9 A-h (b) 176.63 A-h
(c) 797.3 A-h (d) 265.04 A-h

10. Which of the following statements is/are correct? Choose the correct option.

I. H_2O_2 is stored in iron container after addition of stabiliser.

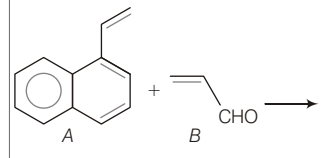
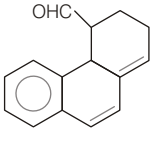
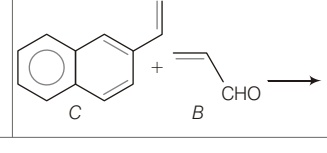
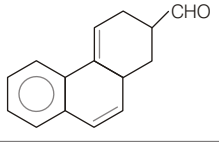
II. Lithium is strongest reducing agent among alkali metals due to its least ionisation energy.

III. Solubility of alkaline earth metal hydroxides increases from $Be(OH)_2$ to $Ba(OH)_2$ because hydration energy > lattice energy.

IV. Among $FeCl_2$, $SnCl_2$, $AlCl_3$ and $MgCl_2$, maximum covalent character is shown by $FeCl_2$ as Fe is a transition metal.

(a) I and II (b) Only III
(c) III and IV (d) Only I

11. Match the following columns.

	Column I (Reactions)	Column II (Final products)
A.		p. 
B.		q. 

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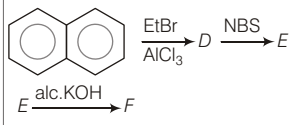
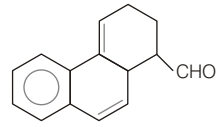
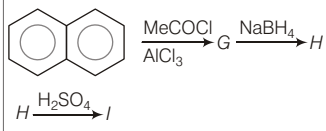
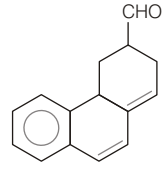
	Column I (Reactions)	Column II (Final products)
C.		r. 
D.		s. 
		t. Product (*A*)
		u. Product (*C*)

Codes

	A	B	C	D		A	B	C	D
(a)	p,s	t	u	q,r	*(b)*	q,r	p,s	t	u
(c)	p,s	q,r	u	t	*(d)*	t	u	p,s	q,r

12. How much $Ca(OH)_2$ in mg will be precipitated, when 500 mL of saturated solution of $Ca(OH)_2$ is mixed with equal volume of 0.4 M NaOH?

$K_{sp}(Ca(OH)_2) = 4.42 \times 10^{-5}$ at 25°C.

(a) 758.944 mg *(b)* 894.115 mg
(c) 722.333 mg *(d)* 816.277 mg

13. Fill in the blanks. Choose the correct order.

P. Increasing order of dipole moments is …*A*… .
I. toluene II. *o*-dichlorobenzene
III. *m*-dichlorobenzene IV. *p*-dichlorobenzene
Q. The isotones of $^{76}_{32}Ge$ are …*B*… .
R. Among H_2S, SiH_4, NH_3 and BF_3 bond angles increase in the order as …*C*… .
S. C-atoms in $C_2(CN)_4$ are …*D*… hybridised.

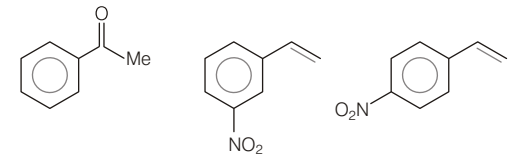
	A	B	C	D
(a)	IV<I<III<II	$^{77}_{33}As$ and $^{78}_{34}Se$	$H_2S < NH_3 < SiH_4 < BF_3$	*sp* and sp^2
(b)	I<II<III<IV	$^{77}_{32}Ge$ and $^{77}_{34}Se$	$H_2S < NH_3 < BF_3 < SiH_4$	*sp*
(c)	I<IV<III<II	$^{77}_{32}Ge$ and $^{77}_{33}As$	$NH_3 < H_2S < SiH_4 < BF_3$	sp^2
(d)	IV<I<II<III	$^{77}_{34}Se$ and $^{78}_{34}Se$	$H_2S < SiH_4 < NH_3 < BF_3$	*sp*, sp^2 and sp^3

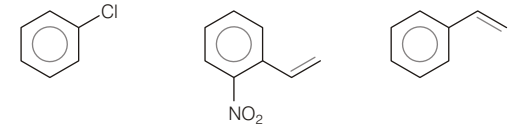
14. Complete the following reaction. Choose the correct option.

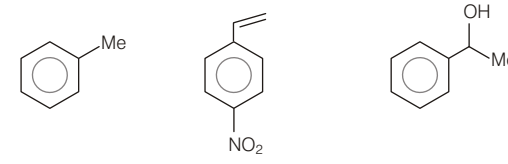
I. $C_6H_6 + \underset{A}{MeCOCl} \xrightarrow{AlCl_3} B \xrightarrow[H_2SO_4]{HNO_3} C \xrightarrow{NaBH_4} D \xrightarrow{H_2SO_4} E$

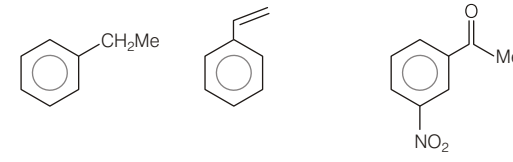
II. $B \xrightarrow{NaBH_4} F \xrightarrow[\Delta]{H_2SO_4} G \xrightarrow[H_2SO_4]{HNO_3} H$

B E H

(a) 

(b) 

(c) 

(d) 

15. At 500K, in a 100 L vessel, 1 mole of N_2 gas and 3 moles of PCl_5 is placed at equilibrium pressure of 2.05 atm. Assuming ideal behaviour, calculate degree of dissociation for PCl_5 and K_p for the reaction.

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

(a) 0.33, 0.204 atm *(b)* 0.45, 0.386 atm
(c) 0.66, 0.295 atm *(d)* 0.99, 0.857 atm

16. Which of the following statements are correct? Choose the correct option.

I. Plumbosolvency refers to oxidation of lead in air to lead oxide.
II. Zone refining of metals is based on the principle of greater solubility of pure metal than that of impurity.
III. Lead has been placed in qualitative group analysis Ist and IInd because it forms insoluble $PbCl_2$ and PbS and its salts are partly soluble in water.
IV. Addition of $SnCl_2$ to $HgCl_2$ gives white precipitate which turns into grey precipitate.
V. Dust and mist are the particulate air pollutants.
VI. Eutrophication of a lake means, it has excess amount of organic matter.

(a) I, II and III *(b)* IV, V and VI
(c) I, II and V *(d)* III, IV, V and VI

17. Fill in the blanks. Choose the correct option.

I. The maximum number of 90° angle between bond pair-bond pair of electrons is observed in…*A*…hybridisation.
II. …*B*…has maximum number of lone pair of electrons on the central atom.

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III. …*C*… exhibits diamagnetic behaviour.

IV. Pair of …*D*… has the same bond order.

	A	B	C	D
(a)	sp^3d	XeF_4	NO	NO^+ and CN^+
(b)	dsp^2	ClO_3^-	O_2^+	CN^- and CN^+
(c)	sp^3d^2	I_3^-	O_2^{2-}	CN^- and NO^+
(d)	dsp^3	SF_4	O_2	O_2^- and CN^+

18. Match the products of (Column I) with their precursors in (Column II).

	Column I		Column II
A.	Perspex	p.	Salicylic acid
B.	Orlon	q.	Methyl methacrylate
C.	Salol	s.	Resorcinol Phthalein
D.	Fluorescein	r.	Prop-2-ene nitrile

Codes

	A	B	C	D		A	B	C	D
(a)	s	r	q	p	*(b)*	p	q	r	s
(c)	q	r	p	s	*(d)*	r	p	s	q

19. Which of the following statements are true? Choose the correct option.

I. 15 lines in the spectrum will be observed, when electrons return from 7th shell to 2nd shell.

II. The Zeeman effect involves splitting of spectral lines of frequency ν_0 into three components.

III. Orbital angular momentum of *f*-electrons is $\sqrt{12}$.

IV. The minimum repulsive energy between two electrons in the ground state of helium atom is 27.2 eV.

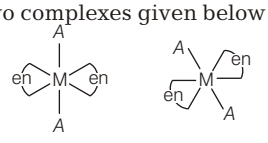
	I	II	III	IV		I	II	III	IV
(a)	T	T	T	T	*(b)*	F	F	F	F
(c)	T	F	T	F	*(d)*	F	T	F	T

20. Fill in the blanks. Choose the correct option.

I. The effective atomic number (EAN) of Ni in $Ni(CO)_4$ is …. .

II. The correct name of $(CO)_3Fe{<}^{CO}_{CO}{>}^{CO}_{CO}Fe(CO)_3$ is …. .

III. The two complexes given below are …. .



	I	II	III
(a)	38	hexacarbonyl iron (III) μ-tricarbonyl ferrate (0)	geometrical isomers
(b)	54	tricarbonyl iron (0) μ-tricarbonyl iron (0) tricarbonyl	position isomers
(c)	28	*bis*-tricarbonyl-μ- tricarbonyl iron (0)	optical isomers
(d)	36	tri-μ-carbonyl *bis*-(tricarbonyl) iron (0)	identical

21. Select the correct pairs. Choose the correct option.

I. Raffinose → a trisaccharide.

II. α-glucose and β-glucose → epimers.

III. Surfactants and detergents → detergency.

IV. Tributyrin → butyric acid + glycerol.

(a) I and IV *(b)* II and III *(c)* I and III *(d)* II and IV

22. On compressing two moles of an ideal monatomic gas at NTP adiabatically and reversibly, volume occupied is 4.48 dm^3. Given, C_v for ideal gas = 12.45 J/K mol, calculate the value of ΔE.

(a) 24.7 kJ *(b)* 12.7 kJ *(d)* 16.7 kJ *(d)* 44.8 kJ

23. Fill in the blanks. Choose the correct option.

I. $^{235}_{92}U + {}^1_0n \rightarrow ...A... + {}^{92}_{36}Kr + 3{}^1_0n$

II. The probability of survival of a radioactive nucleus for one mean life is …*B*… .

III. 5 mL of 1 M NaCl with coagulating power of …*C*… . is required for the coagulation of 100 mL of arsenious sulphide solution.

IV. The temperature at which the catalytic activity of a catalyst is maximum is called …*D*… . temperature.

	A	B	C	D
(a)	$^{141}_{56}Sr$	e	$\frac{1}{252}$	critical
(b)	$^{141}_{56}La$	$\frac{2}{e}$	$\frac{1}{30.5}$	room
(c)	$^{141}_{56}Cs$	$\frac{e}{2}$	$\frac{1}{38.8}$	absolute
(d)	$^{141}_{56}Ba$	$\frac{1}{e}$	$\frac{1}{47.6}$	optimum

24. Fill in the blanks. Choose the correct option.

I. $CH_3CH_2CH_2Br \xrightarrow{X} \text{Product} \xrightarrow{Y} (CH_3)_2CHBr$.
X and *Y* are …*A*… .

II. …*B*… gives positive iodoform test upon reaction with I_2 and NaOH.

III. Isobutyl magnesium bromide with dry ether and ethyl alcohol gives …*C*… .

IV. ……is formed when methylamine is heated with chloroform in the presence of KOH.

	A	B	C	D
(a)	*X* = conc. alc. NaOH at 80°C *Y* = HBr/acetic acid at 20°C	$PhCHOHCH_3$	$(CH_3)_3CH$ and CH_3CH_2OMgBr	CH_3NC
(b)	*X* = dil. NaOH at 20°C *Y* = HBr/acetic acid at 20°C	$H_5C_2\underset{\displaystyle OH}{\underset{\vert}{C}}HC_2H_5$	$(CH_3)_2CHCH_2CH_2CH_3$ + Mg(OH)Br	CH_3NC
(c)	*X* = dil. *aq.* NaOH at 20°C *Y* = $Br_2/CHCl_3$ at 0°C	$C_6H_5CH_2CH_2OH$	$(CH_3)_3CH$ and Mg(OH)Br	CH_3CN
(d)	*X* = conc. alc. NaOH at 80°C *Y* = $Br_2/CHCl_3$ at 0°C	$H_3C\underset{\displaystyle CH_3}{\underset{\vert}{C}}HCH_2OH$	$(CH_3)_2CHCH_2OH$ and CH_3CH_2MgBr	CH_3NHCH_3

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25. Which of the following statements are correct regarding gaseous states of matter?

I. At high temperature and pressure $Z > 1$, this fact can be explained by van der Waals' equation when the constant b is negligible but not a.

II. Most probable speed increases with increase in temperature whereas fraction of total molecules with most probable velocity decreases.

III. Gas A can be liquefied at room temperature by applying pressure but gas B cannot because critical temperature of B is greater than that of A.

IV. If the absolute temperature of a gas in a fixed volume is quadrupled, then the velocity in initial and final state would be related as $v_f = 2v_i$.

(a) I and III *(b)* II and III *(c)* III and IV *(d)* II and IV

26. Match the crystalline solids in (Column I) with packing arrangement in (Column II).

	Column I	Column II
A.	CaF_2	p. Cations are in ccp arrangement.
B.	NaCl	q. Anions are in tetrahedral voids.
C.	ZnS	r. Anions are in ccp arrangement.
D.	Na_2O	s. Cations are in octahedral voids.

Codes

	A	B	C	D
(a)	p	q	r	s
(b)	p,q	r,s	r	r
(c)	p,r	q,s	s	r
(d)	r,s	p,r	q	q

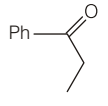
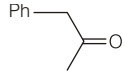
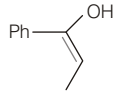
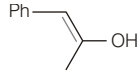
27. Fill in the blanks. Choose the correct option.

I. 1-butyne and 2-butyne can be distinguished by …A… .

II. $Ph-C\equiv C-CH_3 \xrightarrow{Hg^{2+}/H^+} B$ … .

III. …C… + HBr → 2, 2-dibromopropane.

IV. Ozonolysis of an organic compound gives formaldehyde as one of the products. This confirms the presence of …D… .

	A	B	C	D
(a)	Ammonical Cu_2Cl_2		$CH_3-C\equiv CH$	a vinyl group
(b)	Br_2, CCl_4		$CH_3-CH=CH_2$	two ethylenic double bond
(c)	H_2, Lindlar's catalyst		$CH_3-HC=CHBr$	an isopropyl group
(d)	dil. H_2SO_4, $HgSO_4$		$HC\equiv CH$	an acetylenic triple bond

28. Match the redox titrations in (Column I) with their equivalent weights in (Column II).

	Column I	Column II
A.	$KMnO_4$ *vs* oxalic acid	p. $\left(\frac{M}{6}, \frac{M}{1}\right)$
B.	$KMnO_4$ *vs* ferrous ammonium sulphate	q. $\left(\frac{M}{5}, \frac{M}{2}\right)$
C.	$K_2Cr_2O_7$ *vs* ferrous ammonium sulphate	r. $\left(\frac{M}{1}, \frac{M}{2}\right)$
D.	$Na_2S_2O_3$ *vs* iodine (I_2)	s. $\left(\frac{M}{5}, \frac{M}{1}\right)$

Codes

	A	B	C	D
(a)	p	q	s	t
(b)	q	s	p	r
(c)	t	s	q	p
(d)	s	r	q	p

29. A sample of sea water is found to contains 7% NaCl and 0.26% $MgCl_2$ by mass. The normal boiling water is 100°C and K_b(water) = 0.51 K kg/mol. Calculate the normal boiling point of sample of sea water assuming that both the salts are completely ionised.

(a) 111. 36°C

(b) 103.38°C

(c) 106.38°C

(d) 101.36°C

30. Fill in the blanks. Choose the correct option.

I. The number of isomers for the compound with molecular formula $C_2BrClFI$ is …A… .

II. The order of leaving group ability is …B… .

—OAc, — OMe, —OSO_2Me, —OSO_2CF_3

(i) (ii) (iii) (iv)

III. Out of F^-, OH^-, CH_3^-, NH_2^-, …C… has the highest nucleophilicity.

IV. The IUPAC name of is …D… .

	A	B	C	D
(a)	6	(iv) > (iii) > (i) > (ii)	CH_3^-	bicyclo-2, 1, 0-pentane
(b)	5	(i) > (ii) > (iii) > (iv)	F^-	1, 2-cyclopropyl cyclobutane
(c)	4	(iii) > (ii) > (i) > (iv)	OH^-	cyclopentane-4, 3-annulene
(d)	3	(ii) > (iii) > (iv) > (i)	NH_2^-	1, 2-methylene cyclobutane

Answers

1. (a)	**2.** (a)	**3.** (a)	**4.** (a)	**5.** (d)	**6.** (c)	**7.** (d)	**8.** (a)	**9.** (d)	**10.** (b)
11. (b)	**12.** (a)	**13.** (a)	**14.** (a)	**15.** (a)	**16.** (d)	**17.** (c)	**18.** (c)	**19.** (a)	**20.** (d)
21. (a)	**22.** (a)	**23.** (d)	**24.** (a)	**25.** (d)	**26.** (b)	**27.** (a)	**28.** (b)	**29.** (d)	**30.** (a)

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Questions to Measure Your Problem Solving Skills

Paper 1

One or More than One Option Correct Type

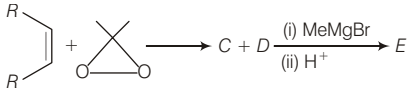
1. The reaction(s) possessing diamagnetic product is/are

(a) $K_2Cr_2O_7$ 2KOH C H_2O

(b) CrO_2Cl_2 NaCl H_2O A 2HCl

(c) Mn $2HNO_3$ P H_2

(d) $Na_3[Fe(CN)_6]$ NO Q NaCN

2. 

The product D is

(a) propanoic acid *(b)* acetone

(c) ethyl methyl ketone *(d)* ethanol

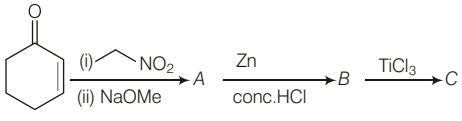
3. The product exhibiting ionisation isomerism in which of the following reactions?

(a) $[Co(NH_3)_5Br]^{2+} + BaSO_4$ P

(b) $[Cd(H_2O)_4Br_2] + Br$ $[Cd(H_2O)_3Br_3] + H_2O$

(c) $[Co(NH_3)_5Cl]^{2+} + H_2O$ Q Cl

(d) $[Cr(H_2O)_4Cl_2]$ Cl $2H_2O$ R

4. 

(a) B is a carboxylic acid

(b) C is an enolisable ketone

(c) Step A to B is Clemmensen reduction

(d) $TiCl_3$ acts as an oxidising agent

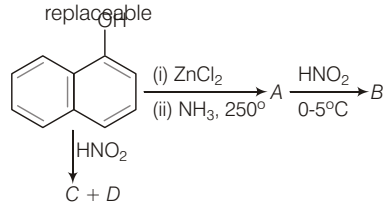
5. When dichloro dimethyl silane undergoes hydrolysis gives P, which undergoes dehydration upon heating forms Q? Choose the correct statements about this reaction sequence.

(a) Q is a linear polymer having —Si_2O— linkage

(b) P is very stable compound which cannot be dissociated

(c) P is dihydroxy derivative of silicon compound

(d) In dichloro dimethyl silane Si—Cl bond is very weak and replaceable

6. 

Which of the following statements is/are correct for the above transformations?

(a) $ZnCl_2$ acts as a Lewis acid

(b) Conversion of A to B possesses $\overset{+}{N}O_2$ as intermediate

(c) C and D are aromatic compounds

(d) Product A has enolisable proton at atleast one carbon-atom in the aromatic ring

7. Consider the following unbalanced equation,

MnO_4 H_2O_2 H_2SO_4

$MnSO_4$ K_2SO_4 O_2 H_2O

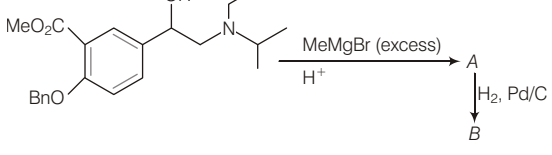
The correct statements for the balanced equation are

(a) MnO_4 is reduced

(b) H_2O_2 is oxidised

(c) 8 water molecules have been formed

(d) K_2SO_4 is one of the byproducts

8. 

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(a) H_2, Pd/C reduces benzyl amine to simple amine
(b) Grignard reagent undergoes reaction with —OBn group
(c) *A* upon heating loses water molecule
(d) H_2, Pb/C deprotects OBn to OH

9. When 4.0 A of current is passed throught a 1.0 L solution of 0.10 M $Fe^{3+}(aq)$ for 1.0 h, it is partly reduced to Fe(*s*) and Fe^{2} (*aq*). The correct statements are
(a) 0.025 mole of Fe(s) will be deposited
(b) 0.075 mole of Fe remains as Fe^{2}
(c) 0.050 mole of Fe remains as Fe^{2}
(d) 0.10 mole of electrons are required to convert all Fe^{3} to Fe^{2}

10. A salt *AB*, when dissolves in water in an isolated beaker, temperature of the solution decreases. What can be concluded accurately for this dissolution process?
(a) It is usual phenomena for all salts
(b) *AB* can be salt of heavy metal
(c) The dissolution process is exothermic
(d) Lattice energy is greater than the hydration energy

Integer Type Questions

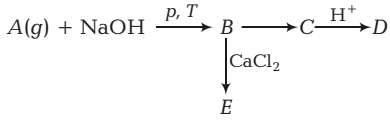
11. IO_2F_2 has trigonal bipyramidal geometry. How many lone pair(s) is/are lost to convert its geometry to *see-saw*?

12. A flask containing $F_2(g)$ at a concentration of 0.024 M is allowed to come in equilibrium with F(*g*) as

$F_2(g) \rightleftharpoons 2F(g)$; K_p 9.6 10^{3} atm at 1000K

Calculate the equilibrium concentrations of F gas in the multiple of 10^{3} approximately, once the equilibrium has been established?

13.

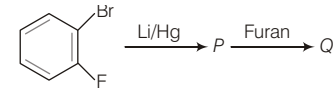


How many double bonds are present in product *E*?

14. Addition of 3.0 g of a non-volatile solute to 100 g of CCl_4 raises boiling point of CCl_4 by 0.6 K, K_b 5.03 and K_f for CCl_4 is 31.8. Calculate depression in freezing point approximately.

15. Calculate the mass (in gram) of available O_2 per litre is present in a solution of H_2O_2, 10 mL of this solution requires 25 mL of *N* / 20 $KMnO_4$ for complete oxidation of it.

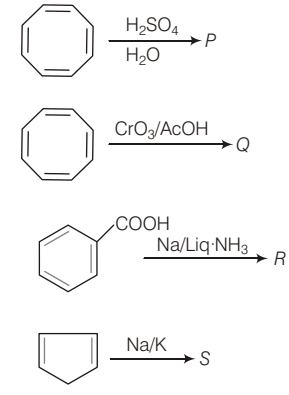
16. How many conjugated double bonds are present in product *Q* in the following reaction?



17. The energy corresponding to one of the lines in the Paschen series for H-atom is 18.16 10^{20} J. The quantum numbers for the transition which produced this line is

18. How many moles of nitrogen is/are evolved, when excess of ammonia reacts with Cl_2 and HCl separately?

19. In how many reactions, products are obtained as aromatic compounds?

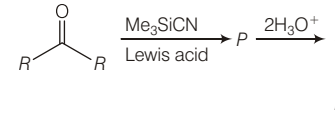


20. The mineral hawleyite, a form of CdS, crystallises in one of the cubic lattice with edge length of 5.87Å. If density of mineral is 4.63 g/cm^3 and Schottky defect is 0.098 g/cm^3. Calculate the number of unit cells.

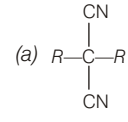
Paper 2

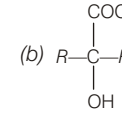
Single Option Correct Type

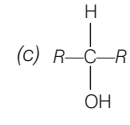
1.



Product *R* is

(a) 

(b) 

(c) 

(d) RCH_2 CHO

2. The ionisation constant of HIO_3 is 0.20 at 25°C. If 0.20 g pure crystals of NaOH are added to a 100 mL of 0.10 M HIO_3 solution at 25°C, following neutralisation reaction occurs, NaOH + HIO_3 $NaIO_3$ H_2O

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What would be the pH of the resulting solution?
(a) 7 (b) 1.45
(c) 2.75 (d) 8

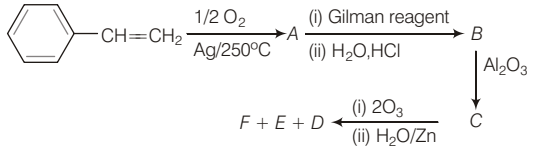
3. An unknown alkyl bromide (C_4H_9Br), reacts with Na to give an alkane C_8H_{18}. This alkane is shown to be identical to that obtained by the Kolbe's electrolysis of the sodium salt of the acid Me_2CHCH_2COOH. The alkyl bromide would be
(a) 1-bromo -2-methylpropane
(b) 2-bromo-3-methylbutane
(c) 1-bromo-3-methylbutane
(d) 3-bromo-1-methylbutane

4. Consider the following reactions,

$$2XeF_6 + SiO_2 \longrightarrow P + SiF_4$$
$$P \xrightarrow{4H_2O} Q + 8HF$$

Choose the correct statement from the following.
(a) *P* has square pyramidal while *Q* has *see-saw* structure
(b) *P* and *Q* both have two lone-pairs of electron on their central metal atom
(c) *P* has 4 sigma bonds and *Q* has two-sigma bonds
(d) Lone pair does not affect the structure of these two compounds

5. A compound *P* forms an unstable pale blue colour solution in water which rapidly decomposes even in the cold. The solution acts as reducing agent and decolourises bromine water and an acidified solution of $KMnO_4$. It also oxidises $SnCl_2$ in dil.HCl solution. The compound *P* would be
(a) HNO_3 (b) HNO_2 (c) NO_2 (d) N_2O

6. 

Choose the correct option from the following
(a) *C* is a conjugated compound
(b) *B* contains an amine group
(c) *A* is an acid derivative
(d) *E* is benzophenone

7. Sucrose Glucose + Fructose

Above reaction takes place at 308 K in 0.5N HCl. At time zero, the initial total rotation of the mixture is 32.4 . After 10 min, the total rotation is 28.8°. If the rotation per mole of sucrose, glucose and fructose are 85 , 74 and 86.04 respectively, what would be the half-life of the reaction if reaction is of first order?
(a) 11.69 min (b) 117.4 min (c) 1160 min (d) 1200 min

8. Which pair of the complex compounds acts as a reducing agent?
(a) $(Cp)_2Fe, Mn(CO)_4$
(b) $[Mn(CO)_6], [Co(NH_3)_4(PPh_3)_2]$
(c) $(Cp)_2Cr(NO)$, $[Co(NH_3)_4(CO)]$
(d) $(Cp)_2Ni, [Mn(CO)_5]$

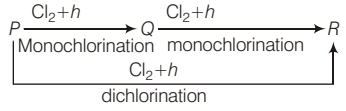
9. What will form, when the reduction of glucosone takes place by Zn and CH_3COOH?
(a) Glucose (b) Fructose
(c) Glucosazone (d) Arabinose

10. Choose the incorrect option from the following.
(a) In oxihalides of sulphur bond order of S O bond varies as $SOBr_2 < SOCl_2 < SOF_2$
(b) O O bond length in ozone is more than in O_2
(c) Sugar turns blue on addition of conc. H_2SO_4
(d) $KMnO_4$ should not dissolve in conc. H_2SO_4

Comprehension Type

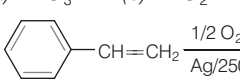
Passage 1

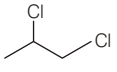
15 mL of gaseous hydrocarbon *P* requires 357 mL of air for complete combustion and gaseous products obtained occupy 327 mL volume. Assume all volumes measured at STP.



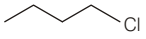
11. The molecular formula of the hydrocarbon *P* is
(a) C_3H_7 (b) C_3H_8 (c) C_4H_{10} (d) C_2H_6

12. Which isomer of *R* on reaction with diethylmalonate (DEM) will give cyclobutane derivative?

(a) 

(b) 

(c)

(d) 

Passage 2

The electrolytic solution shows abnormal colligative properties. To account for this fact we define a quantity called as van't Hoff factor and it is written as,

$$i = \frac{\text{Actual number of particles in solution after dissociation}}{\text{Number of formula units initially dissolved in solution}}$$

i 1 (for non-electrolytes)
i 1 (for electrolytes, undergoing dissociation)
i 1 (for solutes, undergoing association)

13. Benzoic acid undergoes dimerisation in benzene solution. The van't Hoff factor (i) is related to the degree of association ' ' of the acid as
(a) *i* 1 $\frac{}{2}$ (b) $i = 1 + \frac{}{3}$ (c) $i = 2$ (d) $i = 1 \frac{}{2}$

14. 0.1 M $K_4[Fe(CN)_6]$ is 40% ionised. What will be its van't Hoff factor?

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(a) 0.26 (b) 2.6 (c) 3.6 (d) 0.36

Passage 3

An acid *A* is pale-blue liquid. The potassium salt of this acid does not give any reaction with $BaCl_2$ but gives white crystalline precipitate *B* with Ag^+ ions. The acid *A* reacts with urea to liberate two gases *C* and *D*. Gas *D* is used in synthesis of urea also. On adding thiourea in acid *A* followed by addition of $FeCl_3$/dil.HCl red coloured substance *E* is obtained.

15. Compound *E* contains how many unpaired electron(s)?

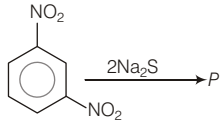
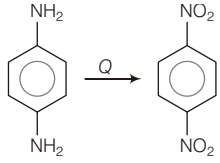
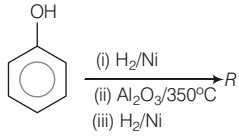
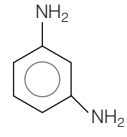
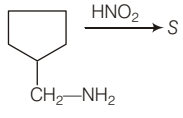
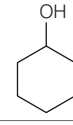
(a) 5 (b) 2 (c) 4 (d) 0

16. Gas *D* is responsible for

(a) sweet odour of rose (b) global warming
(c) production of methane (d) burning of carbon

Matching Type Questions

17. Match the following.

	Column I	Column II
A.		p. CF_3CO_3H
B.		q.
C.		r. 
D.		s. 

Codes

	A	B	C	D
(a)	r	p	s	q
(c)	s	q	p	r

	A	B	C	D
(b)	p	r	s	q
(d)	r	p	q	s

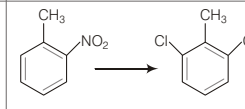
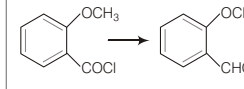
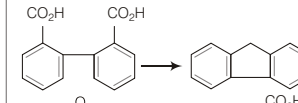
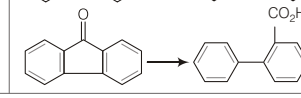
18. Match the following

Column I	Column II
A. $M^{2+} + K_2CrO_4 \rightarrow$ Yellow ppt.	p. Li
B. Metal $+ NH_3 \rightarrow$ Bronze solution	q. Mg
C. MCl_2 + conc. $H_2SO_4 \rightarrow$ White ppt.	r. Ba
D. $M(SO_4)_x \rightarrow SO_3 + M_2O_x$	s. Na

Codes

	A	B	C	D
(a)	r	p,q	s	q, r
(b)	p	q	s,r	p, r
(c)	r	p, q, r, s	r	p, q, r
(d)	q	p, q, r, s	p, q	q

19. Match the following

	Column I (Reactions)	Column II (Reagents)
A.		p. Ca-salt, Zn|NaOH, Zn|Hg HCl
B.		q. KOH
C.		r. Cl_2|Fe, Fe|HCl, $\frac{NaNO_2}{HCl}$ CuCl|HCl
D.		s. $LiAlH_4$, N_2O_4

Codes

	A	B	C	D
(a)	r	p	s	q
(c)	s	p	r	q

	A	B	C	D
(b)	r	s	p	q
(d)	s	q	r	p

20. Match the following

Column I	Column II
A. Butter of tin	p. Mg_2SiO_4
B. Sugar of lead	q. PbO
C. Litharge	r. $SnCl_4 \times 5H_2O$
D. Olivine	s. $Pb(CH_3COO)_2$

Codes

	A	B	C	D
(a)	r	q	s	p
(c)	s	r	p	q

	A	B	C	D
(b)	r	s	q	p
(d)	p	q	r	s

Answers

Paper 1

1. (a,b,d)	**2.** (c)	**3.** (a,c)	**4.** (b,c,d)	**5.** (a,b,d)	**6.** (a,c)	**7.** (a,b,c,d)	**8.** (a,c,d)	**9.** (a,b,d)	**10.** (b,d)
11. (1)	**12.** (2)	**13.** (2)	**14.** (4)	**15.** (2)	**16.** (3)	**17.** (6)	**18.** (1)	**19.** (3)	**20.** (4)

Paper 2

1. (c)	**2.** (b)	**3.** (a)	**4.** (a)	**5.** (b)	**6.** (a)	**7.** (b)	**8.** (c)	**9.** (b)	**10.** (c)
11. (b)	**12.** (a)	**13.** (d)	**14.** (b)	**15.** (a)	**16.** (b)	**17.** (d)	**18.** (c)	**19.** (b)	**20.** (b)

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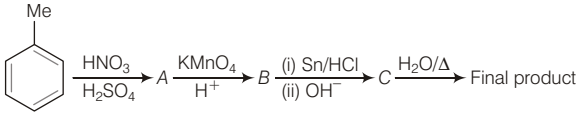
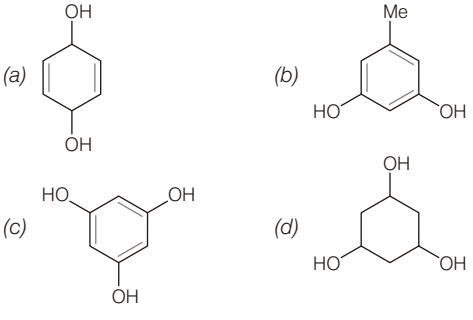
35 Best Questions on Alcohols, Phenols And Ethers *for Medical Entrances*

1. The most effective pair of reagents for the preparation of *tert*-butyl ether is
(a) *tert*-butyl alcohol and ethyl bromide
(b) sodium ethoxide and *tert*-butyl bromide
(c) potassium *tert*-butoxide and ethanol
(d) potassium *tert*-butoxide and ethyl bromide

2. Select the incorrect statement.
(a) When solution of 3-buten-2-ol in aqueous sulphuric acid is allowed to stand for one week it was found to contain both 3-buten-2-ol and 2-buten-1-ol
(b) Solvolysis of $(CH_3)_2C{=}CH{-}CH_2{-}Cl$ in ethanol is lower than alkyl chlorine
(c) $CH_3{-}CH{=}CH{-}CH_2{-}OH$ when reacts with HBr give a mixture of 1-bromo-2-butene and 3-bromo-1-butene
(d) All of the above

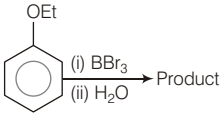
3. Identify the final product in the following reaction sequence





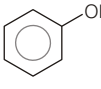
4. Butane-1, 2, 3-triol undergoes oxidation cleavage by HIO_4. During this process
(a) 2 equivalents of HIO_4 consumed and 2 equivalents of HCOOH and 1 equivalent of $CH_3CH{=}O$ is formed
(b) 1 equivalent of HIO_4 consumed and HCOOH and $CH_3COCOOH$ are formed
(c) 2 equivalents of HIO_4 consumed and HCOOH, $HCH{=}O$ and $CH_3{-}CH{=}O$ are formed
(d) 3 equivalents of HIO_4 consumed and 2 equivalents HCOOH and 1 equivalent of CH_3COOH are formed

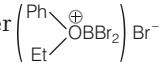
5. Which of the following statements is/are correct about the following reaction?



I. The products are $+C_2H_5OH + H_3BO_3$.

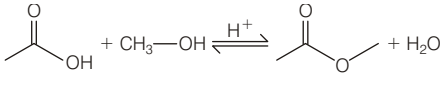
II. The liberated Br^- attacks Et, displacing $PhOBBr_2$, which is ultimately hydrolysed to give the products.

III. The products are  $+C_2H_5Br + H_3BO_3$.

IV. BBr_3 plays a role similar to the H in HI by forming a complex with the ether 

(a) I and II
(b) II, III and IV
(c) I, II and IV
(d) Only IV

6. What is true for the equilibrium reaction?



(a) Removal of water will increase the amount of ester at equilibrium
(b) Application of pressure increases the amount of ester at equilibrium
(c) The use of equimolar quantities of CH_3OH and CH_3COOH will give the greatest yield of the ester at equilibrium
(d) Addition of CH_3COOCH_3 will cause the formation of equal number of moles of water

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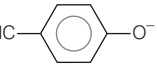
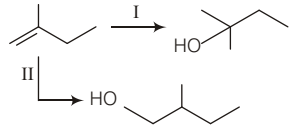
7. Which of the following statements is incorrect?

(a) Acid-catalysed esterification of PhOH is faster than *p*-nitrophenol with MeCOOH

(b) Base-catalysed hydrolysis of *p*-nitrophenyl acetate is faster than phenyl acetate.

(c) The reaction of PhO^- is slower than  with $PhCH_2Cl$

(d) The nitration of phenol is faster than phenyl acetate

8. 

Which of the following option is correct for I and II?

(a) I-Oxymercuration-demercuration and Markownikoff's addition
II- Hydroboration-oxidation and anti-Markownikoff's addition

(b) I-Oxymercuration-demercuration and anti-Markownikoff's addition
II-Hydroboration-oxidation and Markownikoff's addition

(c) I-Hydration and direct addition
II-Hydroboration-oxidation and anti-Markownikoff's addition

(d) I- Hydration and Markownikoff's addition
II-Oxymercuration-demercuration and anti-Markownikoff's addition

9. Choose the correct option for following statements.

I. $CH_2=CHOCH_3$ can be readily cleaved by dilute acids to a mixture of a carbonyl compound and an alcohol but $CH_3CH_2OCH_3$ does not.

II. When $CH_3CH_2OCH_3$ is treated with conc.HI, two products are obtained.

(a) Only I *(b)* Only II *(c)* I and I *(d)* None of these

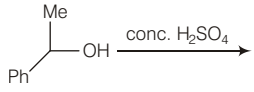
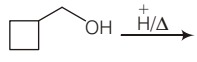
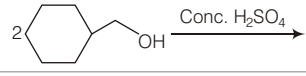
10. Choose the correct option for following statements.

I. Both phenol and salicylic acid on treatment with excess bromine give 2, 4, 6,-tribromo-phenol.

II. When phenol is treated with excess Br_2 at an elevated temperature, a compound having formula $C_6H_3Br_3O$ is obtained.

(a) Only I *(b)* Only II
(c) I and II *(d)* None of these

11. Match the Column I with Column II.

Column I	Column II
A. 	p. Ring expansion
B. 	q. Intramolecular dehydration
C. 	r. Dimerisation

Codes

	A	B	C
(a)	q	r	p
(b)	q	p	r
(c)	p	q	r
(d)	r	p	q

12. $(CH_3)_3C-O-CH_3$ reacts with HI in anhydrous condition and in aqueous condition to give different set of products.

The products respectively are

(a) $(CH_3)_3CI + CH_3OH$; $CH_3I + (CH_3)_3COH$

(b) $(CH_3)_3CI + CH_3CH_2OH$; $CH_3I + (CH_3)_2CHOH$

(c) $CH_3I + (CH_3)_3COH$; $(CH_3)_3CI + CH_3OH$

(d) None of the above

13. Which of the following statements is incorrect for the conversion of *ROH* to *RX* by reagent $SOCl_2$ compared to using HX?

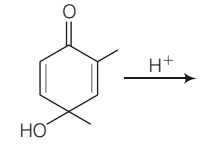
(a) $SOCl_2$ must be used in aqueous condition

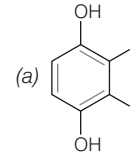
(b) Stereochemistry does not change by $SOCl_2$

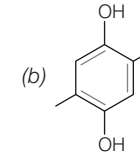
(c) $SOCl_2$ is not useful for 3° alcohol, while HX reacts easily with 3° alcohol involving no rearrangement

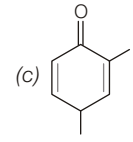
(d) Reaction between *ROH* and $SOCl_2$ undergo S_Ni reaction

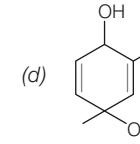
14. Identify the major product formed from the following reaction.



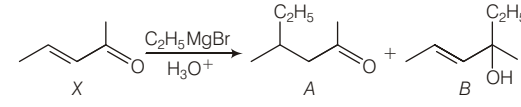
(a) 

(b) 

(c) 

(d) 

15. Formation of *A* and *B*, when *X* reacts with C_2H_5MgBr.



This is due to

I. 1, 2-addition to give *B*.

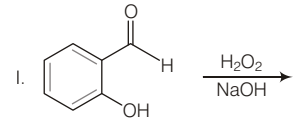
II. 1, 4-addition to give enolic compound which tautomerises to give *A*.

III. Formation of carbanion to give *A* and *B*.

IV. C_2H_5MgBr abstracts H-atom from *X*.

(a) I and II *(b)* II and IV
(c) I and III *(d)* III and IV

16. Which of the following reactions will give catechol as the final product?

I. 

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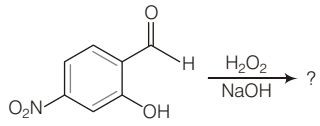
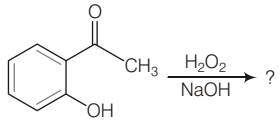
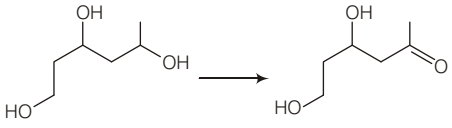
II. 

III. 

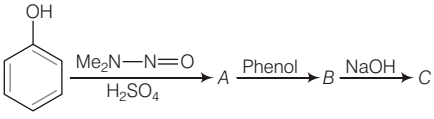
(a) Only I *(b)* Only II
(c) I and III *(d)* I and II

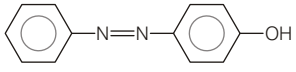
17. Polyhydroxy compound *A* is oxidised to *B* as shown below:

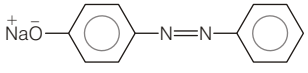


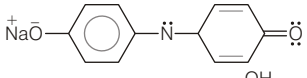
The correct statement for the steps involved is
(a) addition of alkaline $KMnO_4$
(b) addition of acetone
(c) protection of other hydroxyl groups by acetal formation using acetaldehyde.
(d) elimination of H_2O molecules

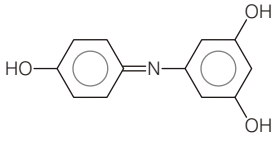
18. Identify the product of the following transformation.



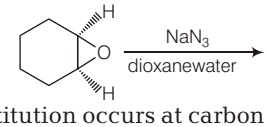
(a) 

(b) 

(c) 

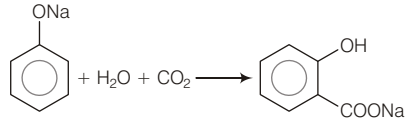
(d) 

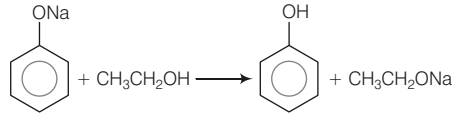
19. In the following reaction,

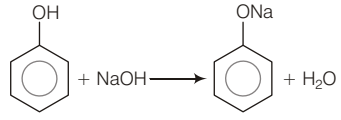


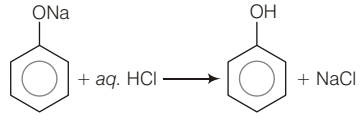
I. Substitution occurs at carbon with inversion of configuration.
II. Product is *trans*-2-azidocyclohexanol.
III. Configuration at the attacking carbon is retained.
IV. Product is *cis*-2-azidocyclohexanol.
(a) I and II *(b)* II and III *(c)* I and IV *(d)* II and III

20. Which of the following acid-base reactions is not feasible?

(a) 

(b) 

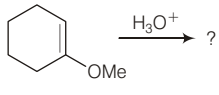
(c) 

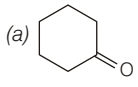
(d) 

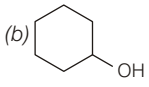
21. Dehydration of alcohols to form alkene is always carried out with conc. H_2SO_4 and not with conc.HCl or HNO_3. This is because
I. Cl^- ion being a good nucleophile will result into substitution reaction.
II. HNO_3 will give eliminated product.
III. HSO_4^- ion being very weak nucleophile cannot result into substitution reaction.
(a) I and III *(b)* Only I *(c)* II and III *(d)* Only II

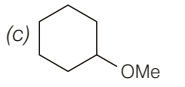
22. Phenol can be prepared by
I. Heating benzenediazonium chloride with dil. H_2SO_4.
II. Hydrolysis of chlorobenzene with *aq.*KOH.
III. Heating sodium salicylate with (NaOH + CaO).
IV. Reacting cumene hydroperoxide with dil. H_2SO_4.
(a) I and II *(b)* I, III and IV
(c) II, III and IV *(d)* I and IV

23. Identify the product of the following transformation.



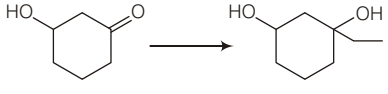
(a) 

(b) 

(c) 

(d) None of these

24. Consider the following transformation.



Which of following statements are correct?

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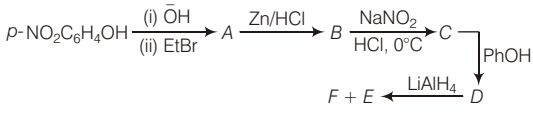
I. First protection of C═O group is done by using glycol.
II. First protection of —OH group is done by using *tert*-butyldimethylsilyl (TBS).
III. Then treatment with C_2H_5MgBr is done followed by hydrolysis.

(a) Only I *(b)* I and II
(c) II and III *(d)* All of these

25. Identify compound (*E*) in the following reaction sequence.



(a) p-EtO C_6H_4OH
(b) p-$H_2NC_6H_4NH_2$
(c) o-EtO C_6H_4OH
(d) p-EtO $C_6H_4NH_2$

26. A compound $C_9H_{12}O$ (*A*), is oxidised under vigorous conditions to benzoic acid. *A* reacts with CrO_3 and gives a positive iodoform test. The correct statement about compound *A*.

I. The compound does not give violet colour on treatment with $FeCl_3$.
II. The compound is a 2° alcohol.
III. The compound is a benzylic alcohol.
IV. The compound is chiral.

(a) I, II, III *(b)* I, III, IV
(c) I, II, IV *(d)* II, III, IV

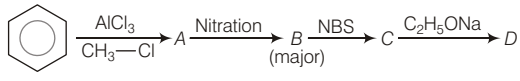
27. When a mixture of ethanol and methanol is heated in the presence of conc.H_2SO_4, the resulting organic product(s) is/are

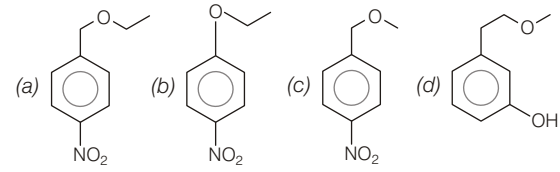
(a) $CH_3OC_2H_5$ and CH_3OCH_3
(b) Only $CH_3OC_2H_5$
(c) $CH_3OC_2H_5$, CH_3OCH_3 and $C_2H_5OC_2H_5$
(d) CH_3OCH_3 and $C_2H_5OC_2H_5$

28. Rectified spirit obtained by fermentation process contains 4.5% of water. In order to remove water, rectified spirit is mixed with suitable quantity of benzene and heated. Benzene helps because

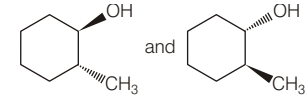
(a) it forms an azeotropic mixture having high boiling point and thus allows the alcohol to distill over
(b) it is dehydrating agent
(c) it forms low boiling azeotropic mixture which distill over, leaving behind pure alcohol which cannot be distilled
(d) it forms the lower layer which retains all the water so the alcohol can be distilled off

29. Identify the product for the following transformation.



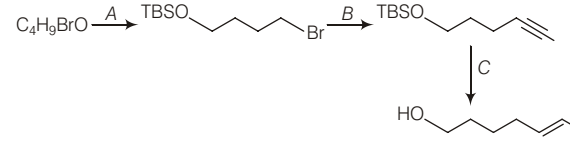


30. Select the best method for the preparation of the following compounds,



(a) Reaction of cyclohexane with BH_3, $NaOH/H_2O_2$, following by CH_3Br
(b) Reaction of cyclohexane with *m*-CPBA, followed by CH_3MgBr/H_3O^+
(c) Reaction of cyclohexanone with CH_3Li
(d) Reaction of 1-methylcyclohexene with CH_3Li.

31. Supply the missing reagent *A* to *C*.

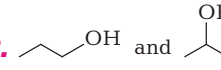


(TBS = *tert*-butyldimethysilyl)

	A	*B*	*C*
(a)	TBSCl/DMF	$Na^+\bar{C} \equiv C—CH_3$	(i) Li, Et_2NH (ii) NH_4Cl (iii)Bu_4NF^-
(b)	TBSCl/DMF	C_2H_5MgBr	(i) Li, Et_2NH (ii) NH_4Cl
(c)	TBS	$ClC \equiv C—CH_3$	(i) NaOH (ii) $Bu_4N^+F^-$
(d)	TBSCl	Bu_4NF	$Bu_4N^+F^-$

32. The cleavage of an aryl-alkyl ether with hydrogen halide will give

(a) a molecule each of phenol and an alkyl halide
(b) a molecule each of an alkyl halide, aryl halide and water
(c) a molecule each of an aryl halide and water
(d) a molecule each of an alkyl halide and water

33. 

can be best distinguished by

(a) oxidation with conc. H_2SO_4 followed by reaction with Tollen's reagent
(b) oxidation by heating with copper followed by reaction with Fehling solution
(c) oxidation with acidic potassium dichromate followed by reaction with Tollen's reagent
(d) oxidation with alk. $KMnO_4$ followed by reaction with Fehling solution

34. THF is formed when 4-chloro-1-butanol is treated with aqueous sodium hydroxide.

Which of the following is incorrect regarding above transformation?

(a) It is an intramolecular S_N2 reaction to form a ring

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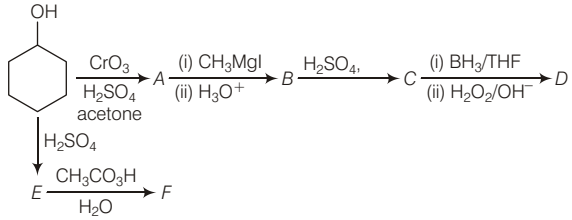
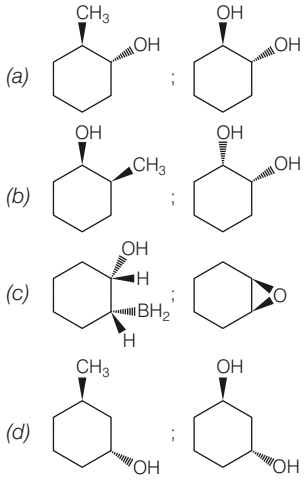
(b) Even though treatment of the alcohol with hydroxide favours a large equilibrium concentration of the alkoxide
(c) The product is a cyclic ether
(d) As alkoxide anions are consumed by the substitution reaction, their equilibrium concentration is replenished by deprotonation of additional alcohol molecules

35. Identify *D* and *F* in the following series of reactions





Answers

1. (d)	**2.** (b)	**3.** (c)	**4.** (c)	**5.** (b)	**6.** (a)	**7.** (c)	**8.** (a)	**9.** (a)	**10.** (c)
11. (b)	**12.** (c)	**13.** (a)	**14.** (b)	**15.** (a)	**16.** (c)	**17.** (c)	**18.** (c)	**19.** (a)	**20.** (b)
21. (a)	**22.** (b)	**23.** (a)	**24.** (c)	**25.** (d)	**26.** (c)	**27.** (c)	**28.** (c)	**29.** (a)	**30.** (b)
31. (a)	**32.** (a)	**33.** (b)	**34.** (b)	**35.** (a)					

Notice Board

JEE Main 2016 Exam Date 3, 9 and 10 April 2016

The official notification of JEE Main 2016 has been released. No more maintaining the suspense, this year, the Joint Entrance Examination (JEE) Main will be held on 3 April 2016, in offline mode, and on 9 and 10 April 2016, in online mode. The application form of it will be released on 1 December 2015 and candidates will be able to avail and submit it till 31st December 2015. Putting all the rumours to rest, the Board has also announced that as always 40:60 weightage mechanic will be used to calculate the rank of the candidates.

JEE Main 2016 Important Dates

Events	Dates
Detailed Information Brochure will be Released on	1 December 2015
Online Registration will Begin in	1 December 2015
The Registration will Close on	31 December 2015
Issuance of Admit Card	3rd Week of March 2016
Dates for JEE Main 2016 1. Offline Exam (Paper 1 and 2) 2. Online paper (Paper 1 only)	3 April 2016 9 and 10 April 2016
JEE Main Official Answers Key will be Released on	3rd Week of April 2016
JEE Main Result will be Announced on	27 April 2016

JEE Main 2016 Schedule

Date of Exam	Paper	Mode of Paper	Timing
3 April 2016	Paper 1 (B.E/B.Tech)	Pen and Pencil (Offline)	9:30 am to 12:30 pm
3 April 2016	Paper 2 (B.Arch/ B.Planning)	Pen and Pencil (Offline)	14:00 pm to 15:00 pm
9 April 2016	Paper 1 (B.E/B.Tech)	Computer Based (Online)	Shift 1: 9:30 am to 12:30 pm Shift 2: 2:00 pm to 5:00pm
10 April 2016	Paper 1 (B.E/B.Tech)	Computer Based (Online)	*will only be held if required

Some Crucial Points to Note

- Candidates who did not pass in qualifying exam in 2013 but retook the exam in 2014 and passed, are not eligible.
- Candidates who did not qualify 10+2 exam in 2015 and are reappearing for it 2016, are required to rewrite the exam of all the 5 subjects.
- The state level exam of Odisha has been scrapped because now JEE Main scores will be considered for admission in the colleges in the state. However, the age limit and the number of attempts will remain the same as the past year. This is not applicable to NITs, IIITs and GFTIs.

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{JEE Advanced Practice}

Single Integer Type Questions on THERMODYNAMICS

A collection of chapterwise best questions of their types

1. The lattice enthalpy of solid KCl is 181 kcal mol ^{1} and the enthalpy of KCl solution in water is 1 kcal mol ^{1}. If the hydration enthalpies of K^+ and Cl ions are in the ratio of 2 : 1 and the enthalpy of hydration of K^+ is 20 ykcal/mol ^{1}. Calculate the value of y.

2. Find the fuel value (per cm^3) of the intimate mixture of ferric oxide and aluminium which is used as fuel in rockets.

Heat of formation and densities are as follow:

$H_f^{\ominus}(Al_2O_3)$ 399 kcal/mol, $H_f^{\ominus}(Fe_2O_3)$ 199 kcal/mol. Density of Fe_2O_3 4 g/cm^3, density of Al = 2g/cm^3.

3. 2 dm^3 of methane under 600 kPa pressure and 300 K and 4 dm^3 of oxygen under 900 kPa pressure and 300 K temperature, are forced into 3 dm^3 evacuated vessel, the temperature being maintained at 300 K. Assuming that these gases are ideal and the change in entropy of gases is xJK ^{1}. Find the value of x.

4. The heat of combustion of glucose is 2880 kJ/mol. 25% of this energy is available for muscular work. If for walking 1 km, 100 kJ muscular work is done, then calculate the maximum distance a person can walk after consuming 120 g of glucose?

5. The diameter of a balloon is 0.5 m which contains air at 25°C and 1 bar pressure. It is then filled with air isothermally and reversibly until the pressure reaches 5 bar. Assuming that pressure is proportional to the diameter of the balloon. The work done in the process is x 10^6 J. Calculate the value of x.

6. The polymerisation of ethylene to polyethylene is represented by the following reaction,

$$n(CH_2 = CH_2) \longrightarrow (CH_2 \quad CH_2)_n$$

where, n has integral value. The average bond energies of C C and C C bonds are 590 and 331 kJ/mol respectively at 298K. The enthalpy of polymerisation is 72 kJ/mol. Find the value of n.

7. 1 mole of NaCl is dissolved in water at 298 K. If lattice energy and solvation energy for NaCl are 777.8 kJ/mol and 774.1kJ / mol and S for the process is 0.043 kJ/mol. Calculate the free energy change for the spontaneous process.

8. The change in enthalpy is x 10^6 J during the heating of 2 kg of -SiO_2 from 300 K to 800 K, if the temperature dependence of heat capacity is given by the equation,

$$C_{p,m} \quad 47 \quad 34 \quad 10^{3}T \quad \frac{11.3 \quad 10^5}{T^2}.$$

Calculate the value of x.

9. Manganese is usually obtained by the reduction of MnO_2 with a strong reducing metal like Al. If standard molar enthalpy of combustion of Mn (s) and Al (s) into their oxides are 521 kJ and 838 kJ respectively. Determine the heat evolved (in the unit of 10^4 J) in the production of 1 kg of Mn from MnO_2.

10. The work done is x kJ, when 50g of iron is dissolved in HCl at 25°C in an open beaker, when the atmospheric pressure is 1 atm. Find the value of x.

11. 2 moles of an ideal gas at 2 atm and 27°C are compressed isothermally to one-half of its volume by an external pressure of 4 atm. Find the value of q in kJ. [Ignore the sign].

12. Find the enthalpy change when infinitely dilute solution of $CaCl_2$ and Na_2CO_3 are mixed.

$_fH^{\ominus}$ for $Ca^{2+}(aq)$, CO_3^{2} (aq) and $CaCO_3(s)$ are 129.80, 161.65 and 288.50 kcal mol ^{1} respectively.

13. The standard Gibbs energies ($_fS^{\ominus}$) for the formation of $SO_2(g)$ and $SO_3(g)$ are 300 and 371 kJ mol ^{1} at 300 K, respectively. Calculate equilibrium constant for the following reaction at 300K in the unit of 10^{24}.

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{JEE Advanced Practice}

14. Calculate the probable molecularity of a perfect gas which undergoes a reversible adiabatic expansion from 27°C, 200 atm to 183 C and 10 atm.

15. An engine which operates in a Carnot cycle absorbs 3 kJ heat at 400°C in a cycle. If it rejects heat at 100°C, the work is done on the engine per cycle is x kJ. Find the value of x to the nearest integer.

16. Find the free energy change (in kJ) when 1 mole of NaCl is dissolved in water at 298K.
Given, lattice energy of NaCl is 778 kJ/mol, hydration energy of NaCl is 774.3 kJ/mol and entropy change at 298K is 43J/mol.
[Ignore the sign of value].

17. Initially at 300K and 10 atm pressure, 1 mole of an ideal gas is allowed to expand adiabatically against a constant pressure of 4 atm until equilibrium is established. Assume the gas to be ideal with C_v 20.75 1.60 10^{-2} T. Calculate the value of S.

18. Find the molar heat capacity of the gas which originally at 1.1 atm and 298K underwent a reversible adiabatic expansion to 1 atm and 287 K.

19. Water is boiled under a pressure of 1 atm. When an electric current of 0.5 A from a 12V supply is passed for 300 s through a resistance in thermal contact with it, it is found that 0.789 g of water is vaporised. The molar internal energy change is x 10^{-1} kJ/mol at boiling point. Find the value of x.

20. 10 g of ice at 0°C is added to 20 g water at 90°C in a thermally insulated flask of negligible heat capacity. Find the S_{system} to the nearest integer, if the heat of fusion of ice is 6 kJ/mol.
[C_p 75.42 J K^{-1} mol^{-1}]

21. 3 moles of an ideal gas is expanded from 2 bar to 1 bar at constant temperature. If the surrounding too are at 1atm and 300K and expansion is against constant external pressure of surroundings, find the entropy change.

22. A sample of 1.0 mole of monoatomic ideal gas at 300 K in a 10 L piston fitted cylinder is expanded, with the surrounding maintained at 300K to 20L adiabatically against a constant external pressure of 0.5 atm, $C_{v,m}$ 1.5R. Calculate, S_{univ} of the process.

23. 1 mole of a monoatomic ideal gas initially at a pressure of 2 bar and a temperature of 273 K is taken to a final pressure of 4 bar by a reversible path defined by pV constant, taking C_v to be equal to 12.5 J $mol^{-1}K^{-1}$. Calculate the value of U / w for this process. [Ignore the sign].

24. G for the dissociation of the dimer ($A_2 \rightleftharpoons 2A$) in benzene solution at 27°C is 6.909 kcal/mol.
If 8 moles of A are dissolved in 10 dm^3 of benzene at 27°C, then the equilibrium concentration of monomer is A 10^{-3}. Calculate the value of A.

25. The bond dissociation energy of XY, X_2 and Y_2 are in the ratio of 1:1:0.5 and H_f of XY is 100 kJ/mol. If the bond dissociation energy of X_2 is 100 a. Find the value of a.

26. The heat of combustion of ethane gas is –368 kcal/mol. Assuming that 60% of heat is useful, how many m^3 of ethane measured at NTP must be burned to supply heat to convert 50 kg of water 10 C to steam at 100 C?

27. The molar heat capacity of methane gas is given by the expression, C_p (17 60 10^{-3} T) J mol^{-1} K^{-1}.
The standard entropy of methane at 300 K is 168 J mol^{-1}. Calculate the entropy of 1 L of methane at 800K and 1 atm.

28. CsOH HCl CsCl H_2O; H 13.4 kcal/mol
CsOH HF CsF H_2O; H 16.4 kcal/mol
The ionisation of HF in H_2O is x kcal. Calculate the value of x.

29. Calculate the moles of butane that must be burnt to heat 10 dm^3 water from 30°C to 100°C. Enthalpy of combustion of butane is 2.879 10^3 kJ/mol .

30. If 2.0 g of helium undergoes a reversible isobaric expansion from 20 to 40 L at 0.8 atm pressure followed by reversible isochoric heating till pressure reaches to 1.0 atm. Calculate the value of H (in kJ).

Answers

1. (6)	**2.** (3)	**3.** (2)	**4.** (5)	**5.** (3)	**6.** (1)	**7.** (9)	**8.** (1)	**9.** (1)	**10.** (2)
11. (5)	**12.** (3)	**13.** (5)	**14.** (1)	**15.** (5)	**16.** (9)	**17.** (3)	**18.** (5)	**19.** (4)	**20.** (3)
21. (5)	**22.** (4)	**23.** (3)	**24.** (2)	**25.** (4)	**26.** (3)	**27.** (3)	**28.** (3)	**29.** (1)	**30.** (6)

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CHEMISTRY SPECTRUM for You

Q1 Dear Sir, whenever onions are sliced or diced or peeled off, tears come out in eyes of people present in the surrounding. What is the reason of this occurrence and how can we prevent our eyes? **(Bhanu Pratap, Saharanpur)**

➥ When an onion is cutted, the cells within the onion break up and release certain volatile sulphur containing compounds. These compounds consist of methionine and cystine which are part of amino acid family. These emitted compounds react with the water of our eyes and forms sulphuric acid. This sulphuric acid causes burning sensation in our eyes and this in turn leads to the tear glands secreating tears.

Tips to prevent our eyes from irritation due to sulphuric acid

- Keep the onions into the refrigerator for atleast 30 to 40 min before cutting. Due to this the reaction rate becomes slower.
- Put the onion into ice-water for a few minutes before cutting.

Cut the onion in half or quarter and soak it into the water. (Amino acids dissolve in water)

- Wear swimming goggles or ski goggles while cutting the onion.
- Use a fan to blow the sulphur containing compounds away.

Note It is the sulphur compound in the onions that also leaves a typical odour of onions on our hands and utensils even after washing.

Q2 Dear Sir, why do we use isotope of carbon for estimating the age of dead persons? Please explain.
(Rajat Singh, Pune)

➥ The age of dead persons is determined by radiocarbon dating. Naturally, occurring carbon contains 98.9% ^{12}C, 1.1% ^{13}C and a tiny amount ($\sim 1 \times 10^{-10}$%) of ^{14}C. ^{14}C is radioactive and has half-life of 5730 yrs. The ^{14}C in all living tissues decay very slowly but is constantly supplied through eating and breathing. Once the person died he was no longer able to renew the ^{14}C in his body. At this point, the amount of ^{14}C in his body started to decrease exponentially with a constant half-life. By determining how much ^{14}C is still present, the age of that person is determined.

Q3 Dear sir, why white powder is spread in an untidy way over the surface of streets, where snow falls? Please explain. **(Shrikant Singh, Meerut)**

➥ The white powder which is spread in an untidy way over the surface of streets, where snow falls is salt. This salt is not the type of salt used for cooking in our homes.

When snow falls, this salt is strewn on the streets to prevent snow from turning into ice. In the night snow accumulates on the streets because the temperature drops to 0°C which is freezing point of water. In the next morning, the streets are slippery due to the ice covering them.

Water containing salt turns into ice at a temperature lower than that of needed for water to turn into ice. That is why, when snow falls, salt strewn on the streets to prevent the snow from turning into ice during the night.

Q4 Dear Sir, how do criminals identify from their fingerprints left at the objects? Please explain.
(Soniya, Dehradoon)

➥ To identify criminals from their fingerprints left at the objects you need a method of making finger-prints visible. Mostly, finger-prints are deposits of sweat, grease and various amino acids and sugars. One way to show up a finger-print is to spray it with ethyl-2-cyanoacrylate, the monomer in superglue.

Hydroxide ions produced from water in the air start the polymerisation of the cyanoacrylate. A white polymer forms along the ridges of the finger-print to give an image of the fingerprint that can be photographed and identified. Mechanism of this reaction is as follows:

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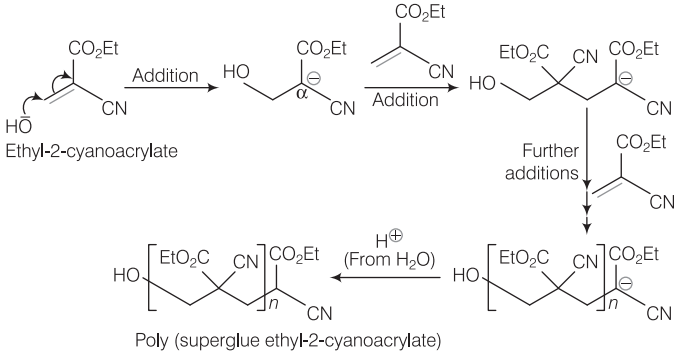

Q4 Dear Sir, most of the time I get confused while solving net entropy change related problems in which phase transitions and temperature change both are involved. Please explain me in an easy way, how can I solve these type of problems?

(Shalini, Saharanpur)

➥ These kinds of problems can be solved easily if you go through stepwise as follow :

Step 1 First write down all the reactions involved in the overall process, keeping in mind that during phase transition, temperature does not change.

Suppose a compound $A(s)$ is heated from T_1° to T_4° C and it changes into $A(g)$, the reactions involve are,

$$\underset{T_1}{A(s)} \longrightarrow \underset{T_2}{A(s)}, \Delta S_1$$

$$\underset{T_2}{A(s)} \xrightarrow{\Delta H_{fusion}} \underset{T_2}{A(l)}, \Delta S_2$$

$$\underset{T_2}{A(l)} \longrightarrow \underset{T_3}{A(l)}, \Delta S_3$$

$$\underset{T_3}{A(l)} \xrightarrow{\Delta H_{vap}} \underset{T_3}{A(g)}, \Delta S_4$$

$$\underset{T_3}{A(g)} \longrightarrow \underset{T_4}{A(g)}, \Delta S_5$$

where, ΔS_1, ΔS_2, ΔS_3, ΔS_4 and ΔS_5 are entropy change for corresponding reactions.

ΔH_{fusion} = Heat of fusion; ΔH_{vap} = Heat of vaporisation

Step 2 For different conditions apply different formulae to calculate entropy change.

(i) At constant pressure, when temperature changes,

$$\Delta S = 2.303 n C_p \log \frac{T_2}{T_1}$$

(ii) At constant volume, when temperature changes,

$$\Delta S = 2.303 n C_V \log \frac{T_2}{T_1}$$

(iii) At constant temperature, when volume changes,

$$\Delta S = 2.303 n R \log \frac{V_2}{V_1}$$

(iv) At constant volume if both temperature and pressure change,

$$\Delta S = 2.303 \left(nC_V \log \frac{T_2}{T_1} + nR \log \frac{p_1}{p_2} \right)$$

(v) At constant pressure, if both temperature and volume change,

$$\Delta S = 2.303 \left(nC_p \log \frac{T_2}{T_1} + nR \log \frac{V_2}{V_1} \right)$$

(vi) If phase change occurs during the process

$$\Delta S = \frac{\Delta H}{T}$$

For solid to liquid phase change, $\Delta H = \Delta H_{fusion}$

For liquid to vapour phase change, $\Delta H = \Delta H_{vap}$

Step 3 Calculate the total entropy change,

$$\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3 + \Delta S_4 + \Delta S_5$$

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JEE Final Touch

Fast Track Revision

Solid State

CLASSIFICATION OF SOLIDS AND CRYSTAL STRUCTURES

Solid state is the state of matter that is characterised by rigidity, incompressibility and mechanical strength of solids. In solid state, the constituent particles (atoms, molecules or ions) are closely packed, have minimum energy and very small intermolecular distances.

On the basis of arrangement of constituent particles, solids are of the following two types:

Property	Crystalline solids	Amorphous solids
Geometry	Arrangement of constituent particles is regular and long order. Hence, possess definite and regular geometry.	Arrangement of constituent particles is irregular and short order. Hence, do not possess definite geometry.
Melting point	Have sharp melting points.	Do not have sharp melting points.
Nature	Anisotropic (different properties in different directions of the crystal) in nature.	Isotropic (same properties in all directions of solid) in nature.
Cleavage	On cutting with sharp knife, give regular cut.	On cutting with sharp knife, give irregular cut.
Heat of fusion	Have characteristic heat of fusion	Do not have characteristic heat of fusion
Examples	Crystals of NaCl, CaF_2 etc.	Rubber, glass etc.

Classification of Crystalline Solids

These are of following four types:

(i) **Molecular solids** These have constituent particles as molecules. These molecules may be bonded by either of van der Waals' forces (e.g. H_2, Cl_2) or dipole-dipole force of attraction (e.g. HCl, SO_2) or strong hydrogen bonds (e.g. H_2O, NH_3).

(ii) **Ionic solids** These have constituent particles as cations and anions. These ions are bonded together by strong electrostatic force of attraction, e.g. NaCl, KNO_3 etc.

(iii) **Covalent solids** These have constituent particles as non-metal atoms linked to adjacent atoms by covalent bond. e.g. diamond, graphite etc.

(iv) **Metallic solids** These have constituent particles as positively charged metal ions (kernals) and free electrons. These constituent particles are bonded each other by metallic bond. e.g. all metals and alloys.

Allotropy

Allotropy is a phenomena, in which two or more different forms of an element exist in the same physical state.

It is a common phenomena shown by metals, metalloids and non-metals.

In the gaseous or liquid state, allotropes most often differ from one another in molecular formula while solid allotropes may differ from one another in their bonding pattern.

Diamond, graphite and Buckminster fullerene are allotropes of solid carbon.

White tin, the stable form of solid tin at 25°C, shows metallic bonding and has properties we associate with metals, when it is kept at low temperatures for long periods of time, it crumbles to powdery grey tin, which has the covalent network structure of diamond.

Phosphorus forms a variety of allotropic forms in solid state, e.g. red phosphorus (P_x, x = very large number), white phosphorus (P_4).

Sulphur has two allotropes named as rhombic and monoclinic, both allotropes have same molecular formula (S_8), but differ in crystal structure.

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IMPORTANT POINTS

- Any material can be made amorphous or glassy either by rapidly cooling its melted form or freezing its vapour, e.g. SiO_2 crystallises as quartz in which SiO_4 (tetrahedral) are linked in a regular manner but on melting and then rapidly cooling, it gives glass in which SiO_4 (tetrahedral) are randomly arranged.

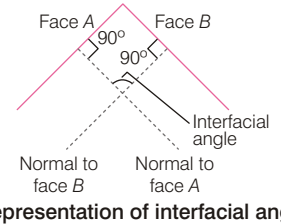
$$SiO_2 \xrightarrow{\text{Melt and rapid cooling}} SiO_2$$

Quartz [SiO_4 unit regularly arranged] → Glass [SiO_4 unit randomly arranged]

- Glass of window panes of some very old houses become thick at bottom and thin at the top because particles of glass flow under the effect of gravity just like liquid.
- Glass objects obtained from historic source appear milky instead of being transparent because transparency is a property generally associated with amorphous character. Glass objects in the day time face sunlight and higher temperature whereas during night the temperature decreases. Due to temperature variation, the particles of glass undergo movement and rearrange themselves to acquire some crystalline character. So, glass objects become milky.
- Amorphous silica has been found to be the best material for converting sunlight into electricity (in photovoltaic cell).

External Features of a Crystal Structure

- **Faces** Crystals are bounded by planar surfaces arranged in definite pattern called 'faces'. Faces are of two types named as like and unlike faces, with similar and different faces respectively.
- **Forms** All faces corresponding to a crystal constitute a 'form'. The form may be simple (in like faces) or combination (in unlike faces) type.
- **Edge and solid angle** The intersection of two faces constitute an edge and when three or more edges intersect they form a solid angle.
- **Interfacial angle** The angle between the normals of the two intersecting faces is called interfacial angle.



Representation of interfacial angle

The faces, edges and interfacial angles are related as,

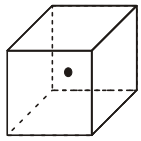
$$f + c = e + 2$$

where, f = number of faces
e = number of edges
c = number of interfacial angles

Zone and zone-axis The faces of a crystal occur in sets. These sets are called **zones**. Each zone forms a complete belt around a crystal. A line drawn through the centre of a crystal in a direction parallel to the edges of a zone is known as zone axis.

Types of Symmetry in Crystals

All crystals of same substance possess the same element of symmetry. A crystalline substance has the following three types of symmetry

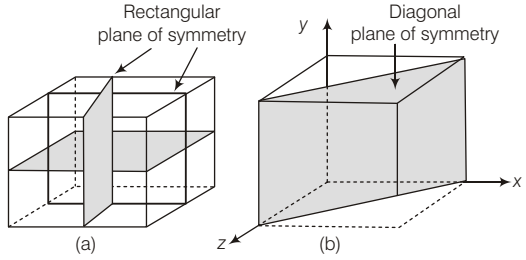


Centre of symmetry (one)

(i) **Centre of symmetry** An imaginary point within a crystal through which if we draw any line, intersects the surface of crystal at equal distances in all directions.

(ii) **Plane of symmetry** It is an imaginary plane passing through the crystal that divides the crystal structure into two equal half.

In a crystal structure, two different types of plane of symmetry are present as shown below.

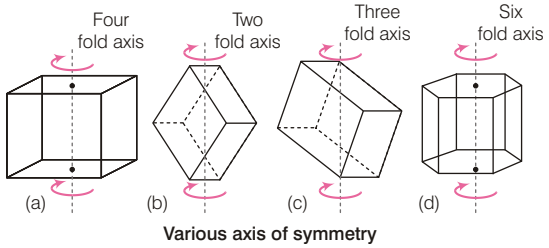


Rectangular and diagonal planes of symmetry

(iii) **Axis of symmetry** It is an imaginary line passing through the crystal, along which if a crystal is rotated, the same appearance is repeated more than once in a complete revolution.

The number of times the appearance is repeated is given by $n = \frac{360°}{\theta°}$,

where, $\theta°$ = the angle of rotation after which the θ crystal structure is repeated and the symmetry is called **n-fold axis of symmetry.**



Various axis of symmetry

Elements of Symmetry

The sum of the numbers of planes, axis and centre of symmetries possessed by a crystal is known as elements of symmetry of a crystal.

e.g. For cubic crystals, plane of symmetry = 3 + 6 = 9

Axis of symmetry = 3 + 4 + 6 = 13

Centre of symmetry = 1

Total elements symmetry

= 9 + 13 + 1 = 23

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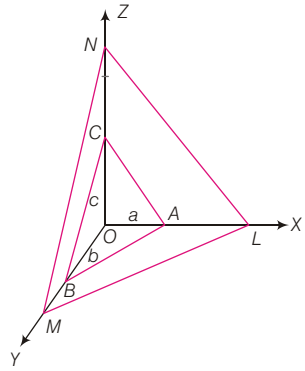
{JEE FINAL TOUCH}

Hay's Law of Rotationality of Angles

According to this law, the intercept of planes of various faces of a crystal along a crystallographic axes are either equal to their unit intercepts (intercept made by unit plane) or a small integer or fractional multiple of them. e.g. in the figure given below the intercepts of the plane *LMN* are at distances 2*a*, 2*b* and 3*c* respectively, where 2, 2, 3 are called Weiss indices.



The intercepts of a crystallographic plane

As the value of Weiss indices can also be ∞, it is represented in terms of Miller indices which is obtained by multiplying the reciprocal of Weiss indices with the *LCM*.

Weiss indices	2	2	3
Reciprocal of Weiss indices	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{3}$
Miller indices	3	3	2

Thus, the face is represented as (332) in this case.

In general, if we represent a face by *hkl*, the perpendicular distance d_{hkl} of the face from the origin is given as $\frac{1}{d_{hkl}} = \sqrt{\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}}$

For cubic system, $a = b = c$

$\therefore \quad d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$

Bragg's Law

According to this law, when a beam of monochromatic X-ray strikes two planes of atoms in a crystal at a certain angle θ and reflected, the intensity of the reflected beam is maximum when

$n\lambda = 2d\sin\theta$ (for constructive interference)

$n\lambda = 4d \sin\theta$ (for destructive interference)

when, n = order of diffraction ($n\varepsilon I^+$)

when, $n = 1$

⊳ first order diffraction

$n = 2$

⊳ second order diffraction.

d = distance between two planes

λ = wavelength of X-rays

θ = angle between X-rays and plane of crystal (angle of diffraction)

Determination of structures of solids by X-ray crystallography

X-ray crystallography is a powerful method for determining the structure of a crystalline solid.

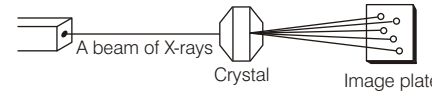
This technique relies on the fact that the spacing between atoms is similar in magnitude to the wavelength of X-rays.

The electron clouds of the atoms in the crystal scatter the X-rays, with the degree of scattering proportional to the atomic number *Z*.

In a crystal, the individual atoms, ions or molecules all lie in identical positions, so they scatter the X-rays in an identical manner.

In a modern instrument, the scattering leads to a **diffraction pattern**, i.e. observed as a series of spots on an image plate.

From this diffraction pattern, the electron density in the crystal can be reconstructed using a computer. This allows the bond length and bond angle data to be determined.



Best Practice SHOTS

1. Which of the following conditions favours the existence of a substance in the solid state?

(a) High temperature (b) Low temperature

(c) High thermal energy (d) Weak cohesive forces

2. Which of the following is not a characteristic of a crystalline solid?

(a) Definite and characteristic heat of fusion

(b) Isotropic nature

(c) A regular periodically repeated pattern of arrangement of constituent particles in the entire crystal

(d) A true solid

3. Which of the following is an amorphous solid?

(a) Graphite

(b) Quartz glass (SiO_2)

(c) Chrome alum

(d) Silicon carbide

4. Which of the following is true about the value of refractive index of quartz glass?

(a) Same in all directions

(b) Different in different directions

(c) Cannot be measured

(d) Always zero

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5. The sharp melting point of crystalline solids is due to
(a) a regular arrangement of constituent particles observed over a short distance in the crystal lattice
(b) a regular arrangement of constituent particles observed over a long distance in the crystal lattice
(c) same arrangement of constituent particles in different directions
(d) different arrangement of constituent particles in different directions

6. Iodine molecules are held in the crystals lattice by
(a) London forces (b) Dipole-dipole interaction
(c) Covalent bonds (d) Coulombic forces

7. Which of the following solids is not an electrical conductor?
I. Mg(*s*) II. TiO(*s*) III. $I_2(s)$ IV. $H_2O(s)$
(a) Only I (b) Only II
(c) III and IV (d) II, III and IV

UNIT CELLS AND PACKING IN SOLIDS

Unit Cell

It is the smallest repeating unit of a crystal which is repeated over and again in different directions, regenerating whole of the crystal. Some important terms related to unit cell are as follows:

1. **Lattice point** The point at which the atoms may present on the unit cell.
2. **Crystal lattice or space lattice** It is the regular repeating arrangement of particles in three dimensional space.
3. **Crystal parameters** A unit cell is described by three edges *a, b* and *c*. These edges may or may not be mutually perpendicular to each other.
   The angles between the edges, α (between *b* and *c*), β (between *c* and *a*) and γ (between *a* and *b*), also describe a unit cell. Thus, *a, b, c* and α, β, γ are six parameters of a unit cell.
4. **Bravais lattice** There are 14 possible three dimensional lattices depending upon the arrangement of atoms present in lattice and parameters of unit cell.

Types of Unit Cell

Unit cells are of the following two types:

(i) **Simple or primitive cubic unit cell** (sc) The unit cell in which the constituent atoms are present only at the corner.

(ii) **Non-primitive or centred unit cell** The unit cell in which atoms present not only at the corners but also at some other positions of the unit cell. These cells may be further divided into the following types:

(a) **Face-centred cubic unit cell** (fcc) The unit cell in which atoms are present at corners as well as faces of unit cell.

(b) **Body-centred cubic unit cell** (bcc) The unit cell in which atoms are present on corners as well as body-centre of unit cell.

(c) **End-centred cubic unit cell** (ecc) The unit cell in which atoms are present at corners as well as centre of any two opposite faces.

Effective Number of Atoms in a Unit Cell

Contribution of atoms, present at different lattice points are different. For a cubic unit cell, atoms present at corners, faces and centre are respectively shared by 8, 2 and 1 unit cells. Hence, for cubic unit cell, number of atoms per unit cell (unit cell constant, Z) is determined by the relation. $Z = \frac{n_c}{8} + \frac{n_f}{2} + \frac{n_i}{1}$

where n_c = number of atoms at the corners of the cube
n_f = number of atoms at six faces of the cube
n_i = number of atoms inside the cube

Number of atoms in different cubic unit cells

Cubic unit cell	n_c	n_f	n_i	Total atoms in unit cell
Simple cubic	8	0	0	1
Body-centred cubic	8	0	1	2
Face-centred cubic	8	6	0	4
End-centred cubic	8	2	0	2

For a hexagonal unit cell, atoms present at corner, edge, face and centre are shared by 6, 3, 2 and 1 unit cells respectively. Hence, for a hexagonal unit cell, the unit cell constant (Z) is given by

$$Z = \frac{N_c}{6} + \frac{N_e}{3} + \frac{N_f}{2} + \frac{N_i}{1}$$

Formulae of atomic radius in different cubic systems

	Atomic Radius (*r*)	Volume of unit cell (*V*)
Simple cubic (sc)	$r = a/2$	a^3
Body-centred cubic (bcc)	$4r = a\sqrt{3}$	a^3
Face-centred cubic (fcc)	$4r = a\sqrt{2}$	a^3
Hexagonal unit cell	$2r = a,\ r = \sqrt{\frac{3}{2}} \times \frac{h}{2}$	$3\sqrt{2}a^3$

In the above table, *a* = edge length and *h* = height of hexagonal.

Crystal System and Bravais Lattices

There are 7 crystal systems and every crystal system does not have all four types of unit cell (one simple and other 3 given above). Hence, there are only 14 types of space lattice corresponding to 7 crystal systems. These are known as Bravais lattices.

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Seven crystal systems

Name of system	Axes	Angles	Bravais lattices
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90°$	Primitive, face-centred, body-centred = 3
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$	Primitive, body-centred = 2
Rhombohedral or trigonal	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$	Primitive = 1
Orthorhombic or rhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$	Primitive, face-centred, body-centred, end-centred = 4
Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90°$, $\beta \neq 90°$	Primitive, end-centred = 2
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90°$	Primitive = 1
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90°$, $\gamma = 120°$	Primitive = 1
			Total = 14 Bravais lattices

Close Packed Structures

- In solids, the constituent particles in solids are close packed in such a way that these occupy maximum available space and leave minimum vacant space.
- Packing in solids is expressed in terms of **packing fraction**

(PF) Packing fraction $= \frac{\text{Total volume of spheres}}{\text{Volume of the unit cell}} \times 100$

The number of spheres surrounding a particular atom is known as **coordination number** (CN).

Packing in solids may be divided into the following categories:

Packing in One Dimension

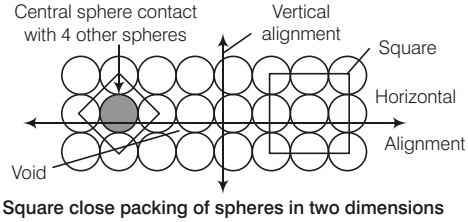
When the atoms are arranged in a row in such a way that these are touching each other is called packing in one dimension.

Packing in Two Dimensions

When atoms are arranged in more than one row by stacking one dimensional closed packed structure is known as two dimensional close packing.

There are two types of two dimensional closed packing:

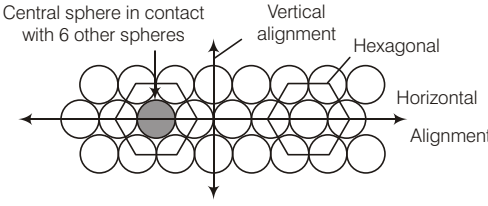
(i) **Square close packing** When atoms arranged in a row is stacked with atoms arranged in another row exactly one over another is known as square close packing.
Coordination number in square close packing = 4



Square close packing of spheres in two dimensions

This is also known as *AAA*...**type arrangement**.

(ii) **Hexagonal close packing** This is generated by placing spheres of the second row in the depressions of first row.
Coordination number in hexagonal closed packing = 6



Hexagonal close packing of spheres in two dimensions

This is also known as *ABAB*... **type arrangement**.

Close Packing in Three Dimensions

The structure obtained by stacking two dimensional layers one above the other is known as three dimensional close packing.

e.g. Mg, Zn, Mo, Be etc.

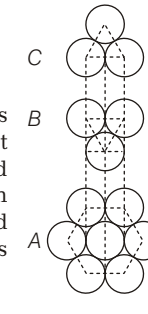
There are two types of three dimensional closed packing:

(i) **Three dimensional closed packing from two dimensional square close packed layers** When two dimensional square close packed layers are arranged exactly one over the other they constitute a three dimensional close packing and arrangement is known as *AAA* **arrangement.** The generated cubic lattice is called simple cubic lattice and unit cell is known as simple or primitive unit cell.

(ii) **Three dimensional close packing from two dimensional hexagonal close packed structure** When hexagonal close packed layers are stacked one over another, they form three dimensional close packing.
When second layer is placed over first layer in depressions, it leads to the formation of three dimension close packed structure. There are two types of arrangements that are possible:

(a) **Hexagonal close packing** When third layer is placed over second layer in such a way that they constitute tetrahedral void, the arrangement is called *ABAB* **pattern,**
e.g. Mg, Zn, Mo and Be.

(b) **Cubic close packing** When the third layer is placed over second layer in such a way that sphere covers octahedral voids, the arrangement is called *ABCABC* **pattern,**
e.g. Fe, Ni, Cu, Ag, Au and Al.



(iii) **Body-centred cubic close packing** Body-centred cubic (bcc) arrangement is obtained when the spheres of the first layer are opened up and spheres of second layer are placed at the top of the hollows in the first layer. The spheres of the third layer are placed exactly above the spheres of first layer. e.g. Li, Na, K, Rb, Cs etc.

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Formulae for calculation of unit cell parameters

Unit cell	Number of atoms per unit cell	Volume of all atoms in a unit cell (v)	Packing fraction $\left(\frac{v}{V}\right)$	Coordination number
sc	1	$\pi\frac{a^3}{6}$	52% $\left(\frac{\pi}{6}\right)$	6
bcc	2	$\frac{\sqrt{3}\pi a^3}{8}$	68% $\left(\frac{\sqrt{3}\pi}{8}\right)$	8
fcc	4	$\frac{\pi a^3}{3\sqrt{2}}$	74% $\left(\frac{\pi}{3\sqrt{2}}\right)$	12
hcp	4	πa^3	74% $\left(\frac{\pi}{3\sqrt{2}}\right)$	12

Density of a Crystal

It can be calculated as density of unit cell by the following formulaes, $d = \frac{\text{mass of all atoms in a unit cell}}{\text{volume of unit cell } (V)}$

$$= \frac{n \times M_0}{N_A} \times \frac{1}{V} = \frac{nM_0}{N_A a^3} \text{ g cm}^{-3}$$

where, n = numbers of atoms in a unit cell

a = edge length of unit cell

M_0 = molecular mass of crystal

$N_A = 6.023 \times 10^{23}$ atoms mol^{-1}

(when, M_0 and a are given in gram and cm respectively)

$$= \frac{nM_0}{N_A a^3} \times 10^{30} \text{ gcm}^{-3}$$

(when, M_0 and a are given in gram and pm respectively).

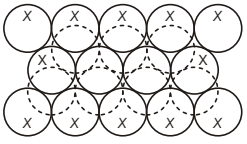
Density of different unit cells

Unit cell type	d in terms of a	d in terms of r
Simple cubic ($n = 1$)	$\frac{M_0}{N_A a^3}$	$\frac{M_0}{8N_A r^3}$
bcc ($n = 2$)	$\frac{2M_0}{N_A a^3}$	$\frac{2M_0}{N_A \times \left(\frac{4r}{\sqrt{3}}\right)^3}$
fcc ($n = 4$)	$\frac{4M_0}{N_A a^3}$	$\frac{4M_0}{N_A \times (2\sqrt{2}r)^3}$
hcp ($n = 6$)	$\frac{6M_0}{3\sqrt{2}a^3 \times N_A}$	$\frac{6M_0}{3\sqrt{2}(2r)^3 N_A}$

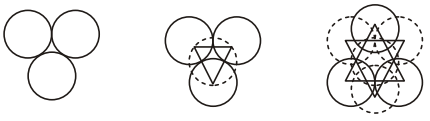
Voids

The empty space between atoms stacked is known as void. There are following three types of voids:

(i) **Trigonal voids** This type of voids exist in two dimensional arrangement (a).



A stack of two layers of close packed spheres and voids



(a) Trigonal void (b) Tetrahedral void (c) Octahedral void

(ii) **Tetrahedral voids** The voids generated by the stacking of four atoms are known as tetrahedral voids *(b)*.

(iii) **Octahedral voids** The voids generated by the stacking of six atoms are known as octahedral voids *(c)*.

Note Number of tetrahedral voids = Number of atoms in ccp × 2 = 2N
Number of octahedral voids = Number of atoms in ccp = N
here, N = Number of atoms in ccp

Relation between radius ratio and coordination number

Radius ratio	Cations occupies	Coordination number	Example
0.155 – 0.225	Trigonal void	3	B_2O_3
0.225 – 0.414	Tetrahedral void	4	ZnS
0.414 – 0.732	Octahedral void	6	NaCl
0.732 – 1.0	Cubic void	8	CsCl

Note A simple cubic unit cell has a single cubic void in the centre.

Radius ratio = $\frac{\text{radius of cation}}{\text{radius of anion}}$

Graphene and its Biological Applications

Graphene is an allotrope of carbon in the form of a two dimensional, atomic scale, hexagonal lattice in which one atom forms each vertex.

It is about 207 times stronger than steel by weight, it conducts heat and electricity efficiently and is nearly transparent.

In 2015 researchers used graphene to create sensitive biosensor by using epitaxial graphene on silicon carbide. These sensors bind to 8-hydroxydeoxyguanosine (8-OHdG) and are capable of selective binding with antibodies. The presence of 8–OHdG in blood, urine and saliva is commonly associated with DNA damage.

If 8–OHdG, levels have been increased in our body, it will cause increased risk of developing several cancers.

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Some Ionic Crystals

Type of ionic crystal	Geometry	Coordination number	Number of formula per UCC	Example
NaCl (1 : 1) (Rock salt type)	ccp: Na^+ → Every element of ccp; Cl^- → At every OHV	6 : 6	$4Na^+ + 4Cl^-$ $4NaCl$ (4)	Halide of Li, Na, K, oxides and sulphides of III A (some exceptions AgF, AgCl, AgBr, NH_4X.
CsCl type (1 : 1)	bcc: Cs^+ → At every corner; Cl^- → At body centred or cubic void	8 : 8	$1Cs^+ + 1Cl^-$ $1CsCl$ (1)	Halides of Cs, TiCl, TiBr, CaS
ZnS type (1 : 1) (Zinc blende type sphalerite)	ccp: Zn^{2+} → Energy element of ccp; S^{2-} → At 50% of THV at alternate tetrahedral void	4: 4	$4Zn^{2+} + 4S^{2-}$ $4ZnS$ (4)	BeS, BeO, CaO, AgI, CuCl, CuBr, CuI
CaF_2 type (1 : 2) (Fluorite type)	ccp: Ca^{2+} → Every element of ccp; F^- → At every THV	$4Ca^{2+}$ $8F^-$ 8 4	$4Ca^{2+} + 8F^-$ $4CaF_2$ (4)	$BaCl_2$, BaF_2 $SrCl_2$, SrF_2, $CaCl_2$, CaF_2
Na_2O type (2 : 1) (Antifluorite)	ccp: Na^+ → At every THV; O^{2-} → Every element of ccp	$8Na^+$ $4O^{2-}$ 4 8	$8Na^+ + 4O^{2-}$ $4Na_2O$ (4)	Li_2O, Li_2S, Na_2O, Na_2S, K_2O, K_2S
ZnS type (1 : 1) (Wurtzite another geometry of ZnS)	hcp: Zn^{2+} → Every element of hcp; S^{2-} → 50% of THV (or at alternate THV)	4 : 4	$6Zn^{2+} + 6S^{2-}$ $6ZnS$ (6)	Same as sphalerite

Best Practice SHOTS

8. Silver forms ccp lattice and X-ray studies of its crystals show that the edge length of its unit cell is 408.6 pm calculate the density of silver (atomic mass = 107.9 u) in gcm^{-3}.
(a) 5.10 *(b)* 1.05 *(c)* 5.79 *(d)* 10.5

9. Which of the following statements is not true about the hexagonal closed packing?
(a) The coordination number is 12
(b) It has 74% packing efficiency
(c) Tetrahedral voids of the second layer are covered by the spheres of the third layer
(d) In this arrangement spheres of the fourth layer are exactly aligned with those of the first layer

10. In which of the following structures coordination number for cations and anions in the packed structure will be same?
(a) Cl^- ions form fcc lattice and Na^+ ions occupy all octahedral voids of the unit cell
(b) Ca^{2+} ions form fcc lattice and F^- ions occupy all the eight tetrahedral voids of the unit cell
(c) O^{2-} ions form fcc lattice and Na^+ ions occupy all the eight tetrahedral voids of the unit cell
(d) S^{2-} ions form fcc lattice and Zn^{2+} ions go into alternate tetrahedral voids of the unit cell

11. In the fluorite structure, the coordination number of Ca^{2+} ion is
(a) 4 *(b)* 6 *(c)* 8 *(d)* 3

12. A solid with high electrical and thermal conductivity is formed from
(a) Si *(b)* Li *(c)* NaCl *(d)* ICl

13. The second order Bragg diffraction of X-rays with λ=1.0 Å from a set of parallel planes in a metal occurs at an angle 60°. The distance between the scattering planes in the crystals is
(a) 0.575 Å *(b)* 1.00 Å *(c)* 2.00 Å *(d)* 1.17 Å
Hint $n\lambda = 2d \sin\theta$; $n = 2$

14. The molar volume of KCl and NaCl are 37.46 mL and 27.94 mL respectively. The ratio of the cubic unit cell edges of the crystals is
(a) 1.296 *(b)* 1.116 *(c)* 1.341 *(d)* 0.950

15. In diamond, the coordination number of carbon is
(a) four and its unit cell has eight carbon atoms
(b) four and its unit cell has six carbon atoms
(c) six and its unit cell has four carbon atoms
(d) four and its unit cell has four carbon atom

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16. A compound formed by elements A and B crystallises in the cubic structure, where, A-atoms are present at the corners of a cube and B-atoms are present at the face-centres. The formula of the compound is

(a) A_2B *(b)* AB_3 *(c)* AB *(d)* A_3B

17. The pyknometric density of sodium chloride crystal is 2.165×10^3 kg m^{-3}, while its X-ray density is 2.178×10^3 kg m^{-3}. The fraction of unoccupied sites in sodium chloride-crystal is

(a) 5.96×10^{-1} *(b)* 5.96×10^{-3} *(c)* 5.96 *(d)* 5.96×10^{-2}

18. A metal crystallises into two cubic phases, face-centred cubic and body-centered cubic, which have unit cell lengths 3.5 and 3.5 Å, respectively. Calculate the ratio of densities of fcc and bcc.

(a) 2.16 : 1 *(b)* 6.39 : 1 *(c)* 1.26 : 1 *(d)* 0.26 : 1

19. An element crystallises in fcc lattice having edge length 400 pm. Calculate the maximum diameter in pm of an atom which can be placed in interstitial site without distorting the structure.

(a) 210.2 *(b)* 110.0 *(c)* 120.2 *(d)* 117.1

20. How many unit cells are present in a cube shaped ideal crystal of NaCl of mass 1.00 g?

(a) 2.57×10^{21} *(b)* 5.14×10^{21} *(c)* 1.28×10^{21} *(d)* 1.71×10^{21}

Hint Mass of one unit cell = $V\times\rho$.

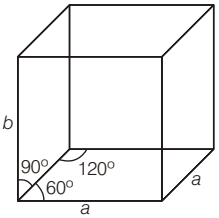
21. Zn converts from its melted state to its solid state, it has hcp structure, then what would be the number of nearest neighbouring atoms?

(a) 6 *(b)* 8 *(c)* 12 *(d)* 4

22. Experimentally it was found that a metal oxide has formula $M_{0.98}O$. Metal M is present as M^{2+} and M^{3+}. Its oxide fraction of the metal which exists as M^{3+} would be

(a) 4.08 % *(b)* 6.05 %
(c) 5.08 % *(d)* 7.01 %

23. Ice crystallises in a hexagonal lattice. At the low temperature the structure was determined and the lattice constants were found to be a=4.53 Å and b=7.41 Å . How many H_2O molecules are contained in a unit cell? (d(ice)=0.92 g/cm^3)?

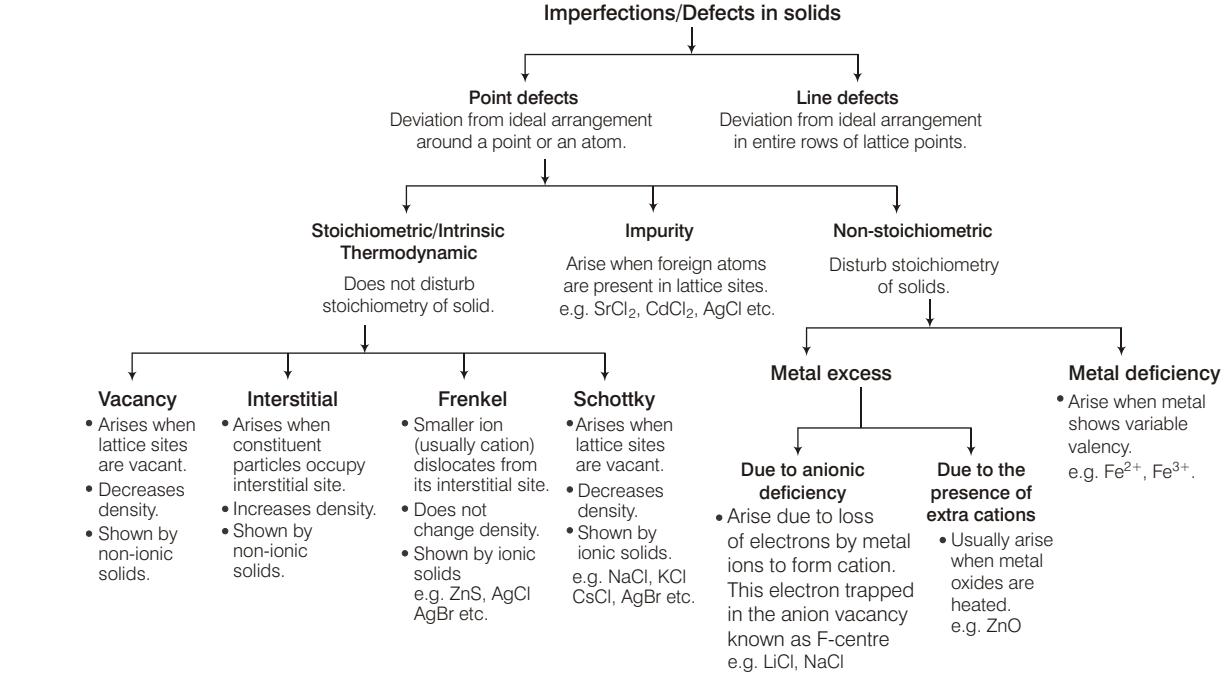


(a) 4 *(b)* 3 *(c)* 2 *(d)* 1

CRYSTAL DEFECTS AND PROPERTIES OF SOLIDS

Imperfections or Defects in Solids

Any deviation from perfectly ordered arrangement of constituents of a solid is known as imperfections or defects in solid.



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Properties of Solids

Some remarkable properties of solids are described below

Electrical Properties of Solids

Depending upon conduction power, solids are divided into the following types

(i) **Conductors** The solids whose conductivity is in the order of 10^7 $(\Omega m)^{-1}$ are termed as conductors. Conductivity is due to the presence of free electrons, e.g. metals.

(ii) **Semiconductors** The solids whose conductivity ranges from 10^{-6} to 10^4 $(\Omega\ m)^{-1}$ are called semiconductors.
e.g. semi-metals.

- ***n*-type semiconductors** Group 14 elements when doped with group 15 elements form *n*-type semiconductors.
- ***p*-type semiconductors** Group 14 elements when doped with group 13 elements form *p*-type semiconductors.

(iii) **Insulators** The solids having conductivity range 10^{-20} to 10^{-10} Ωm^{-1} are known as insulators. e.g. non-metals.

(iv) **Super conductors** The conductor which allow electricity to pass through them without any resistance. The temperature at which a substance starts behaving as superconductor is called **transition temperature**. e.g. $Ba_2Cu_3O_7$ at 90K.

Dielectric Properties of Solids

These are seen in insulators. Insulators show generation of dipoles in them, when they are placed in an electric field. There are the following terms related to dielectric properties of solids.

(i) **Piezoelectricity** It is produced on applying mechanical stress on polar crystals, e.g., Rochelle's salt.

(ii) **Pyroelectricity** It is produced either by heating or cooling some polar crystals, e.g., Cane sugar, lithium sulphate.

(iii) **Ferroelectricity** Piezoelectric crystals with permanent dipoles are said to have ferroelectricity, e.g., $BaTiO_3$, KH_2PO_4, etc.

(iv) **Anti-ferroelectricity** In anti-ferroelectric crystals, the dipoles in alternate polyhedral points up and down in such a way that the crystal does not possess any net dipole moment e.g., $PbZrO_3$. Used in transistor, telephones and computers to prepare small size capacitor of high capacitance.

Types of Magnetic Properties

Properties	Description	Alignment of magnetic dipole	Examples	Applications
Diamagnetic	These are feebly repelled by the magnetic fields due to the existence of paired electron.	All electrons are paired. ↑↓ ↑↓ ↑↓	TiO_2, V_2O_5 NaCl, C_6H_6	Insulator
Paramagnetic	Attracted by magnetic field due to the presence of unpaired electrons, acts as a tiny bar magnet.	At least one unpaired electron. ↑↓ ↑ ↑	O_2, Cu^{2+}, Fe^{3+}, TiO, Ti_2O_3 VO, VO_2, CuO	Electronic applications
Ferromagnetic	Acts as a permanent magnet even after removing magnetic field. Above curie temperature, no ferromagnetism occurs.	All unpaired electrons are in same direction. ↑↑↑↑↑	Fe, Ni, Co, CrO_2	CrO_2 is used in audio and video tapes.
Anti-ferromagnetic	Net dipole moment becomes zero due to equal and opposite alignment.	↑↓ ↑↓ ↑↓	CoO, Co_3O_4 MnO, MnO_2, M_2O_3, FeO, Fe_2O_3, NiO	
Ferrimagnetic	This arises when there is net dipole moment.	↑↓↓↓ ↑↓	Fe_3O_4, Ferrites	

Nanowires

The synthesis of nanowires, nanometre sized atomic assemblies that conduct electricity is a major step in the fabrication of nanodevices.
An important type of nanowires is based on carbon nanotubes, like graphite, can conduct electrons through delocalised π-molecular orbitals that form from unhybridised 2*p*-orbitals on carbon.
Recent studies have shown a correlation between structure and conductivity in single-walled nanotubes (SWNTs) that does not occur in graphite. The SWNT is a semiconductor. If the hexagons are rotated by 90° about their sixfold axis, the resulting SWNT is a metallic conductor.

Direct manipulation of atoms on a surface also leads to the formation of nanowires. The Coulomb attraction between an atom and the tip of scanning tunneling microscope (STM) can be exploited to move atoms along a surface, arranging them into patterns, such as wires.

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Best Practice SHOTS

24. Which of the following point defects are shown by AgBr(*s*) crystals?

I. Schottky defect
II. Frenkel defect
III. Metal excess defect
IV. Metal deficiency defect

(a) I and II *(b)* III and IV *(c)* I and III *(d)* II and IV

25. In which of the following crystals alternate tetrahedral voids are occupied?

(a) NaCl *(b)* ZnS *(c)* CaF_2 *(d)* Na_2O

26. Calcium crystallises in fcc unit cell with a=0.556 nm. What would be the density if it contained 0.1 % Schottky defects?

(a) 1.5463 g / cm^3 *(b)* 1.4962 g / cm^3
(c) 1.5448 g / cm^3 *(d)* 1.5493 g / cm^3

27. Which of the following statements is/are correct? Choose the correct option given below.

I. NaCl and KCl show metal excess defect due to anionic vacancies.
II. *F*-centres are the anionic sites occupied by unpaired electrons.
III. *F*-centres impart yellow colour to the NaCl crystals.

(a) II and III *(b)* Only III
(c) I and II *(d)* All of these

28. Which of the following statements is/are correct?

I. Diode is a combination of *n*-type and *p*-type semiconductor.
II. Diode is used as rectifier.
III. *n*-*p*-*n* and *p*-*n*-*p* are the types of rectifier.
IV. *n*-*p*-*n* and *p*-*n*-*p* are used to detect or amplify radio or audio signals.

Choose the correct option.

(a) I, II and III *(b)* Only I
(c) II, III and IV *(d)* All of these

29. The appearance of colour in solid alkali metal halides is generally due to

(a) *F*-centres *(b)* Schottky defect
(c) Frenkel defect *(d)* Interstitial positions

30. If NaCl is doped with 10^{-4} mol % of $SrCl_2$, the concentration of cation vacancies will be ($N_A = 6.02 \times 10^{23}\ mol^{-1}$)

(a) 6.02×10^{15} mol L^{-1}
(b) 6.02×10^{16} mol L^{-1}
(c) 6.02×10^{17} mol L^{-1}
(d) 6.02×10^{14} mol L^{-1}

31. Which of the following statements is/are correct about metals?

I. Valence band overlaps with conduction band.
II. The gap between valence band and conduction band is negligible.
III. The gap between these bands cannot be determined.
IV. Valence band may remain partially filled.

(a) I, II and III *(b)* I, II and IV *(c)* II and III *(d)* All of these

32. Among the following, which pair is considered to be ferromagnetic?

(a) $MgFe_2O_4$, $ZnFe_2O_4$ *(b)* H_2O, NaCl
(c) Fe, Co *(d)* Ni, MnO

33. Which of the following statements is not correct?

(a) Ferro electricity is due to alignment of dipoles in same direction
(b) Piezo electricity is due to alignment of net dipole moment
(c) Pyro electricity is due to heating polar crystals
(d) $K_4[Fe(CN)_6]$ is a ferro electric compound

34. For N-atoms in a crystal with Ni—interstitial position in its structure is *n*. If there are *n* Frenkel defects in the crystal. The value of 'n' should be

(a) $n = \left(\frac{N_i}{N}\right)^{1/2} e^{E_i/2KT}$ *(b)* $n = \left(\frac{N}{N_i}\right)^{1/2} e^{(E_i/2KT)}$

(c) $n = \left(\frac{N}{N_i}\right)^{1/2} e^{(E_i/2KT)}$ *(d)* $n = \left(\frac{N_i}{N}\right)^{1/2} e^{(E_i/2KT)}$

35. In diamond, if a unit cell of carbon atoms is fcc and hybridisation of carbon is sp^3, then what fraction of voids are occupied by carbon atom?

(a) 75% tetrahedral *(b)* 50% octahedral
(c) 50% tetrahedral *(d)* 75% octahedral

36. Which of the following defects shows decrease in the mass of the crystal lattice?

(a) Frenkel defect
(b) Schottky defect
(c) Edge dislocation
(d) Constitution of *F*-centres

Answers

1. (b)	**2.** (b)	**3.** (b)	**4.** (a)	**5.** (b)	**6.** (a)	**7.** (c)	**8.** (d)	**9.** (d)	**10.** (a)
11. (c)	**12.** (b)	**13.** (d)	**14.** (b)	**15.** (a)	**16.** (b)	**17.** (b)	**18.** (c)	**19.** (d)	**20.** (a)
21. (c)	**22.** (a)	**23.** (a)	**24.** (a)	**25.** (b)	**26.** (c)	**27.** (d)	**28.** (d)	**29.** (a)	**30.** (a)
31. (b)	**32.** (c)	**33.** (d)	**34.** (c)	**35.** (c)	**36.** (b)				

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MASTER STROKES

1. In a spinel structure, oxide ions are cubical closed packed, whereas 1/8th of tetrahedral voids are occupied by *A* ions and 1/2 of octahedral voids are occupied by *B* ions. The charge present on *A* and *B* ions will be

(a) A^{2+}, B^{3+} *(b)* A^{3+}, B^{2+} *(c)* A^{4+}, B^{2-} *(d)* A^{-1}, B^{2-}

2. The first order diffraction of X-rays from a certain set of crystal planes occurs at an angle of 11.8° from the planes. If the planes are 0.281 nm apart. What is the wavelength of X-rays?

(a) 0.281 nm *(b)* 0.2044 nm
(c) 0.1149 nm *(d)* 0.1180 nm

3. A solid $\overset{+}{A}\overset{-}{B}$ have ZnS type structure. When it is heated the ions along with two of the axis passing through the face centre are lost and bivalent ion *(z)* enter here to maintain the electrical neutrality, so that the new formula unit becomes $A_xB_yZ_c$. What is the value of x + y + *c*?

(a) 1 *(b)* 3
(c) 6 *(d)* 7

Hint Number of B^- ions removed

$= 4$ (Two from each face centre) $\times \frac{1}{2}$ (per face centre share) $= 2$

4. Select the false statement for two ionic solids CaO and KI.

(a) KI is soluble in benzene
(b) KI has high melting point
(c) Lattice energy of CaO is much larger than that of KI
(d) CaO has high melting point

5. Which of the following pairs is not isomorphous?

(a) $FeSO_4 \times 7H_2O, MgSO_4 \times 7H_2O$
(b) $NaClO_3, NaNO_3$
(c) $KClO_4, KBF_4$
(d) $BaSO_4, KMnO_4$

Hint The existance of two or more crystalline solids having similar chemical composition in the same crystalline form or structure is called isomorphism, e.g., Na_3PO_4 and Na_3AsO_4.

6. Choose the correct option regarding the limiting value of radius ratio r_+ / r_- is

(a) forces of attraction and repulsion are just equal
(b) forces of attraction are smaller than the forces of repulsion
(c) forces of attraction are larger than the forces of repulsion
(d) None of the above

7. In fcc lattice of NaCl structure, if the diameter of Na^+ is x and the radius of Cl^- is y, then the edge length of NaCl in the crystal is

(a) $3x+2y$ *(b)* $\frac{x}{2}+\frac{y}{3}$ *(c)* $x+2y$ *(d)* $\frac{1}{2}(x+y)$

8. An element has a body-centred cubic structure with a cell edge of 288 pm. The density (ρ) of the element is 7.2 g/ cm^3. What would be the number of atoms which are present in 208 g of the element?

(a) 7.02×10^{24} atoms *(b)* 10.09×10^{25} atoms
(c) 17.04×10^{26} atoms *(d)* 24.16×10^{23} atoms

9. In a solid *AB* having the NaCl structure, *A* atoms occupy the corners of the cubic unit cell. If all the face-centred atoms along one of the axes are removed, then the formula of the solid is

(a) *AB* *(b)* A_7B_{21} *(c)* A_3B_4 *(d)* $A_{3/4}B_{2/3}$

10. In crystals of which one of the following compounds contains maximum distance between centres of cations and anions?

(a) CsI *(b)* LiF *(c)* LiI *(d)* CsF

11. In orthorhombic system of crystal lattice, the value of *a*, *b* and *c* are respectively 4.2Å, 8.6Å and 8.3Å. Molecular mass of solute is 155 g mol^{-1} and that of density is 3.3 g/cc, the number of formula units per cell is

(a) 6 *(b)* 4 *(c)* 1 *(d)* 2

12. A crystal plane makes intercepts *2a*, *2b* and *6c* on the crystallographic axes where *a*, *b*, *c* represent the intercepts of the unit plane. The Miller indices of the plane will be

(a) 113 *(b)* 133 *(c)* 331 *(d)* 332

13. Experimentally, the melting point of RbBr is 682°C while that of NaF is 988°C. The principal reason for this difference in melting point is

(a) the bond in RbBr has more covalent character than the bond in NaF
(b) the internuclear distance $r_c + r_a$ is greater for RbBr than for NaF
(c) the two crystals are not isomorphous
(d) the molar mass of NaF is smaller than that of RbBr

14. The ionic radius of Cl^- ion is 1.81Å. The inter-ionic distances of NaCl and NaF are 2.79 Å and 2.31 Å respectively. The ionic radius of F^- ions will be

(a) 0.78 Å *(b)* 1.33 Å *(c)* 0.23 Å *(d)* 2.34 Å

Answers

1. (a) **2.** (c) **3.** (d) **4.** (a) **5.** (b) **6.** (a) **7.** (c) **8.** (d) **9.** (c) **10.** (a)
11. (b) **12.** (c) **13.** (b) **14.** (b)

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Solutions

TYPES OF SOLUTION, SOLUBILITY AND CONCENTRATION TERMS

It is a homogeneous mixture of two or more substances whose composition can be varied within certain limits. A **solvent** is that component of the binary solution which is present in large amount by mass than the other component termed as **solute.** Solutions in water are called **aqueous solutions** and the solutions in which water does not act as the solvent are called **non-aqueous solutions**. The solvents in the non-aqueous solutions are usually benzene, ether, CCl_4 etc.

Different types of solutions

Types of solutions	Solute	Solvent	Common examples
Gaseous solutions	Gas	Gas	Mixture of nitrogen and oxygen gases, air.
(Homogeneous mixtures)	Liquid	Gas	Chloroform mixed with nitrogen gas.
	Solid	Gas	Camphor in nitrogen gas, dust of smoke-particles in air.
Liquid solutions	Gas	Liquid	Oxygen dissolved in water, CO_2 dissolved in H_2O.
	Liquid	Liquid	Ethanol dissolved in water.
	Solid	Liquid	Sucrose/salt dissolved in water.
Solid solutions	Gas	Solid	Solution of hydrogen in palladium (phenomenon of adsorption of gases over metals).
	Liquid	Solid	Mercury with sodium (amalgams).
	Solid	Solid	Copper dissolved in gold (alloys).

Solubility

Maximum amount of a solute that can be dissolved in a given amount of solvent (usually 100 g) at a given temperature is called solubility at that temperature.

Solubility of Gas in Liquid

All gases are soluble in water and in other liquids upto a greater or lesser extent.

The solubility of a gas depends upon the following factors:

(i) **Nature of the gas** The gases which can be easily liquified are more soluble in common solvents, e.g. CO_2 is more soluble than H_2 and O_2 in water.

(ii) **Nature of the solvent** The gases which are capable of producing ions in aqueous solutions are much more soluble than in other solvent, e.g. gases like NH_3 and HCl are highly soluble in water but not in organic solvents in which they do not ionise.

(iii) **Temperature** As the process of dissolution is an exothermic process, the solubility of gases in general decreases with the increase of temperature.

(iv) **Effect of pressure and Henry's law** According to Henry's law, the solubility(S) of a gas in liquid is directly proportional to pressure(p) of gas over the solution at a definite temperature.

Solubility, $S \propto p$ or $S = Kp$

where, K = proportionality constant

K depends upon the nature of gas, nature of solvent and temperature. The value of K is different for each gas at a particular temperature.

Henry's Law for a Mixture of Two or More Non-reacting Gases

When a mixture of two or more non-reacting gases come in contact with solvent, the mole fraction of the gas in the solution is proportional to the partial pressure of the gas as

$$p = \frac{1}{K'}\chi = K_H\,\chi \qquad \left(K_H = \frac{1}{K'}\right)$$

where, χ = mole fraction of gas.

p = partial pressure of gas

K_H is called Henry's law constant. Different gases have different values of K_H at a definite temperature for a given solvent.

Limitations of Henry's Law

Henry's law holds good only during the following **conditions**:

(i) The temperature should not be very low.
(ii) The pressure should not be very high.
(iii) The gas must not chemically react with the solvent.
(iv) The gases should not associate or dissociate in the solvent.

Haemoglobin
A Henry's Law Deviator

Under normal conditions oxygen gas is sparingly soluble in water. However when oxygen comes in contact with blood in lungs, its solubility increases many fold due to the presence of high concentration of haemoglobin that associate with oxygen molecule.

$$Hb + 4O_2 \rightleftharpoons Hb(O_2)_4.$$

Due to association, Henry's law is not strictly followed in case of solubility of oxygen in blood.

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Applications of Henry's Law

- Soft drinks are sealed at high pressure to increase the solubility of CO_2 in soft drink.
- Rate of respiration increases at high altitude, because, at high altitude, partial pressure of oxygen is low. This results a lowering in the solubility of oxygen in blood. When scuba divers go deep in the sea, solubility of atomospheric gases increases in blood. When they come out to land, the dissolved nitrogen gas come out as bubble feeling painful sensation. To avoid such pain inert He gas is added.

Terms Used for Expressing the Concentration of Solution

- The concentration of a solution is defined as the relative amount of a solute present in a solution.
- The concentration of solution can be calculated as strength in gram per litre (g/L) of solution. Percentage by mass (i.e. mass percentage), percentage by volume (i.e. volume percentage), mole fraction, parts per million (ppm), molarity, molality, formality and in normality.

Best Practice SHOTS

1. The dissolution of ammonium chloride in water is an endothermic reaction. The solubility of this solution
(a) increases on increasing temperature
(b) decreases on decreasing temperature
(c) decreases on increasing temperature
(d) increases on decreasing temperature

2. Aquatic species are more comfortable in cold water rather than in warm because
(a) solubility of gases decreases with increase in temperature
(b) solubility of gases increases with increase in temperature
(c) solubility of gases decreases with decrease in temperature
(d) solubility of a gas in liquid is higher

3. Henry's law constant for the solubility of nitrogen gas in water at 298 K is 1.0×10^{-5} atm. The mole fraction of nitrogen in air is 0.8. The number of moles of nitrogen from air dissolved in 10 mL of water at 298 K and 5 atm pressure is
(a) 4.0×10^{-4} atm *(b)* 4.0×10^{-5} atm
(c) 5.0×10^{-4} atm *(d)* 4.0×10^{-6} atm

4. Concentrated nitric acid used in laboratory work contains 68% nitric acid by mass in aqueous solution. What should be the molarity of such a sample of the nitric acid if the density of the solution is 1.504 gmL^{-1}?
(a) 15.00 M *(b)* 17.00 M *(c)* 16.23 M *(d)* 15.23 M

5. Equal masses of methane and oxygen are mixed in an empty container at 25°C. The fraction of the total pressure exerted by oxygen is
(a) $\frac{2}{3}$ *(b)* $\frac{1}{3} \times \frac{273}{298}$ *(c)* $\frac{1}{3}$ *(d)* $\frac{1}{2}$

6. The molarity of a solution obtained by mixing 750 mL of 0.5 HCl with 250 mL of 2M HCl will be
(a) 0.875 M *(b)* 1.00 M *(c)* 1.75 M *(d)* 0.0975 M

7. The density of a solution prepared by dissolving 120 g of urea (molar mass = 604) in 1000 g of water is 1.15 g/mL. The molarity of the solution is
(a) 0.178 M *(b)* 0.50 M *(c)* 1.02 M *(d)* 2.05 M

8. Concentrated sulphuric acid is approximately 18 M. 58 cm^3 of it is added to water to make 500 cm^3 solution. The normality of the solution will be approximately
(a) 0.18 *(b)* 0.09 *(c)* 0.36 *(d)* 0.27

9. 29.2 (*w*/*w*) HCl stock solution has a density of 1.25% g mL^{-1}. The molecular mass of HCl is 36.5 g mol^{-1}. The volume (mL) of stock solution required to prepare a 200 mL solution of 0.4 HCl is
(a) 2 mL *(b)* 4 mL *(c)* 8 mL *(d)* 6 mL

10. What is the molality of a 13% solution (by weight) of sulphuric acid with a density of 1.02 g/mL ?
(a) 1.232 m *(b)* 1.525 m *(c)* 1.478 m *(d)* 1.025 m

VAPOUR PRESSURE OF SOLUTIONS AND AZEOTROPES

Vapour Pressure of Solutions

The pressure exerted by the vapours over the liquid when it is in equilibrium state at a given temperature is called vapour pressure. Greater the intermolecular force of attraction, lower is the vapour pressure and *vice-versa*. Vapour pressure depends upon *(a)* temperature *(b)* purity of liquids.

1. If a solute is added to the solution, then same molecules of solute replace the molecules of solvent from the surface and lower its vapour pressure.
2. When the solute is volatile, the vapour pressure of the solution depends upon the escaping tendency of the solute molecules from the surface of the solution.
3. When solute is non-volatile then the vapour pressure of the solution decreases because of the decrease in escaping tendency of solvent molecules from the surface.

Raoult's Law

- The partial vapour pressure of a volatile component is directly proportional to its mole fraction in solution.

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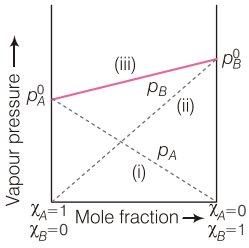
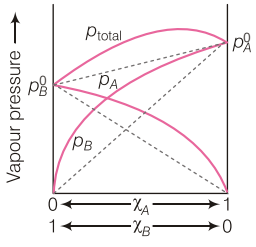
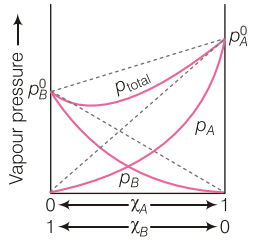
Comparison of Raoult's law between ideal and non-ideal solutions

Ideal solutions	Non-ideal solutions	
	Positive deviation from Raoult's law	Negative deviation from Raoult's law
Obey Raoult's law for any concentration.	Do not obey Raoult's law	Do not obey Raoult's law
Neither heat is evolved nor heat is absorbed ($\Delta H_{mix} = 0$)	Heat is required ($\Delta H_{mix} > 0$)	Heat is evolved (($\Delta H_{mix} < 0$)
There is no change in volume ($\Delta V_{mix} = 0$).	Volume is increased after dissolution ($\Delta V_{mix} > 0$).	Volume is decreased after dissolution ($\Delta V_{mix} < 0$).
The two mixing parts are identical in shape, size and intermolecular force (i.e. $A-A$, $A-B$, $B-B$ interaction should be same).	The two mixing parts have different shape, size and intermolecular force and $A-B$ attractive force is weaker than $A-A$ and $B-B$ attractive forces.	The two mixing parts have different shape, size and intermolecular force. $A-B$ attractive force is stronger than $A-A$ and $B-B$ attractive forces.
Escaping tendency is same before and after mixing.	Escaping tendency increases after mixing, increasing vapour pressure.	Escaping tendency decreases after mixing, decreasing vapour pressure.
$p_A = p_A^0 \chi_A$ $p_B = p_B^0 \chi_B$ $p_T = p_A + p_B$ e.g. chlorobenzene + bromo benzene, benzene + toluene *n*-hexane + *n*-heptane, etc.	$p_A > p_A^0 \chi_A$ $p_B > p_B^0 \chi_B$ $p_T > p_A + p_B$ e.g. Acetone + ethanol, water + ethanol, acetone + CS_2, Acetone + benzene, etc.	$p_A < p_A^0 \chi_A$ $p_B < p_B^0 \chi_B$ $p_T < p_A + p_B$ e.g. Acetone + aniline, acetone + $CHCl_3$, CH_3OH + CH_3COOH, water + HCl, CH_3COOH + pyridine, etc.
		
Plot of solution showing Raoult's law.	Plot of solution showing positive deviation from Raoult's law.	Plot of solution showing negative deviation from Raoult's law.

Limitations of Raoult's Law

(a) It is valid only for very dilute solutions.

(b) It is valid only for the solution having non-volatile and non-electrolyte solute which exist as a single molecule.

(c) It is not valid for those solutes which associate or dissociate in the particular solution.

Vapour Pressure vs Temperature

Vapour pressure of a liquid increases with temperature, as the formation of vapour pressure is an endothermic process.
If p_1 and p_2 are the vapour pressures of a liquid at temperatures T_1 and T_2, then according to **Clausius-Clapeyron** equation.

$$\log_{10}\left(\frac{p_2}{p_1}\right) = \frac{\Delta H_{vap}}{2.030\ R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

If we plot a graph between p, and T the above graphs are obtained.

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Azeotropes
The Constant Boiling Mixtures

- A mixture of two liquids which boils at a constant temperature and distils over without any change in composition is called **azeotropic mixture.**
- Azeotropic mixtures are of two types :
  (a) **Minimum boiling azeotropes** These are the mixtures of two liquids whose boiling point is less than either of the two pure components. These are formed by non-ideal solutions showing positive deviations.
  (b) **Maximum boiling azeotropes** These are the mixtures of two liquids whose boiling point is more than either of the two pure component. These are formed by non-ideal solutions showing negative deviations.
- Example of minimum boiling azeotrope is a mixture of ethanol (95.63% w/w) and water (4.37% w/w) and that of maximum boiling azeotrope is a mixture of HCl (20.2% w/w) and water (79.8% w/w).

Liquid Crystals : A Technology Boon

Liquid crystals have both the properties of solid (directional order of molecules) and liquid (fluidity).

Liquid crystals that change their properties with temperature are called thermotropic liquid crystals. These show the property of a unclear liquid just above the melting point due to the orderly alignment of some molecules. But at higher temperature, the liquid becomes clear. This property is called **mesophase** behaviour of a liquid crystal.

This property was first observed by Austrian biochemist Friedrich Reinitzer in 1988 while studying cholesterol.

Compounds that show mesophases are usually anisotropic. Liquid crystal display (LCD) is a popular example of liquid crystals.

Best Practice SHOTS

11. On mixing 10 mL of acetone with 50 mL of chloroform the total volume of the solution become
(a) < 60 mL *(b)* > 60 mL
(c) = 60 mL *(d)* unpredictable

12. CH_2Cl_2 is more volatile than $CHCl_3$. This concluded that at equilibrium vapour phase will be always rich in the component which is
(a) less volatile *(b)* more volatile
(c) concentrated *(d)* unsaturated

13. In a mixture of *X* and *Y* components show negative deviation when
(a) $\Delta V_{mix} > 0, \Delta S_{mix} > 0$
(b) $\Delta V_{mix} = 0, \Delta V_{mix} > 0$
(c) *A*—*B* interaction is stronger than *A*—*A* and *B*—*B* interaction
(d) *A*—*B* interaction is weaker than *A*—*A* and *B*—*B* interaction

14. In an ideal solution, the intermolecular forces are the same as in the pure components, the enthalpy change of mixing is
(a) negative *(b)* positive *(c)* zero *(d)* one

15. A binary liquid solution is prepared by mixing *n*-heptane and ethanol. Which one of the following statement is correct regarding the behaviour of the solution?
(a) Formed solutions an ideal solution
(b) Solution is non-ideal showing positive deviation from Raoult's law
(c) The solution is non-ideal showing negative deviation from Raoult's law
(d) *n*-heptane shows positive deviation while ethanol show negative deviation from Raoult's law

16. The total pressure (p_{total}) over the solution phase in the container will be the pressure of the component of the solution
(a) Raoult's law
(b) Henry law
(c) Dalton's law of partial pressure
(d) All of the above

17. Which of the following solutions at the same temperature will be isotonic?
(a) 3.42 g of cane sugar in one litre water and 0.18 of glucose in one litre water
(b) 3.42 g of cane sugar in one litre water and 0.18 g of glucose in 0.1 litre water
(c) 3.42 g of cane sugar in one litre water and 0.585 g of NaCl in one litre water
(d) 3.42 g of cane sugar in one litre water and 1.17 g of NaCl in one litre water

18. The mole fraction of toluene in the vapour phase which is in equilibrium with a solution of benzene ($p^\circ_B = 120$ torr) and toluene ($p^\circ_T = 80$ torr) having 2.0 mole of each is
(a) 0.50 *(b)* 0.25 *(c)* 0.60 *(d)* 0.40
Hint: $\chi^1_{T(vap)} = \dfrac{\chi_T p^\circ_T}{\chi_T p^\circ_T + \chi_B p^\circ_B}$

19. When a substance is dissolved in a solvent, the vapour pressure of the solvent is decreased. This results in
(a) an increase in boiling point of the solution
(b) a decrease in the boiling point of the solvent
(c) the solution having a higher freezing point
(d) the solution having a lower osmotic pressure than the solvent

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20. The vapour pressure of a dilute solution of non-volatile solute is p and the vapour pressure of a pure solvent is $p°$. The lowering of the vapour pressure is

(a) positive (b) negative
(c) $p / p°$ (d) $p°/p$

21. Which of the following behaviour is not true for an ideal binary liquid solution?

(a) Plot of p_A *versus* x_A is linear
(b) Plot of p_B *versus* x_B is linear
(c) Plot of p_{total} *versus* x_A (or x_B) is linear
(d) Plot of p_{total} *versus* x_A (or x_B) is non-linear

COLLIGATIVE PROPERTIES

The properties of a dilute solution, which depend only on the number of particles present in the solution are called colligative properties. Hence, these properties are proportional to the number of solute particles in the solution.

The following factors effect the colligative properties in solutions :

(i) Fraction of solute and solvent particles
(ii) Nature of solvent.
(iii) Dissociation and association of solute particles

There are four colligative properties given below :

(a) Relative Lowering of Vapour Pressure

When a non-volatile solute is added to a solvent, the vapour pressure (p) is always less than the vapour pressure of pure solvent ($p°$).

(b) Elevation in Boiling Point of Solvent (Ebullioscopy)

The vapour pressure of a solution decreases on addition of non-volatile solute. Hence, the solution boils at higher temperature than the boiling point of pure solvent, resulting an elevation in boiling point (ΔT_b). The elevation in boiling point is proportional to molality (m) of solution.

(c) Depression in Freezing Point (Cryoscopy)

As the vapour pressure of a solution decreases on addition of a non-volatile solute, the freezing point of solution (T_f) is lower down than the freezing point of pure solvent ($T°_f$) and this lowering in freezing point is proportional to molality (m) of solution.

(d) Osmotic Pressure (π)

It is the external pressure that must be applied to a solution in order to stop the flow of solvent from dilute to concentrated solution through a semipermeable membrane.

Advantages of Osmosis

1. Osmotic pressure measurement provided very good method of determination of molecular mass of polymers like proteins etc., due to the following reasons:
   (i) Osmotic pressure of a solution containing fewer particles is appreciable and therefore can be measured accurately as compared to ΔT_b or ΔT_f which are very small in these conditions.
   (ii) Osmotic pressure is measured at room temperature, hence the method is particularly useful for biomolecules which are generally unstable at higher temperatures.
2. Osmosis plays a vital role in biology also.
   Some of these are :
   (i) For normal functioning of the living systems, the fluid concentration has to be maintained in the plant and animal cells.
   (ii) Movement of water from roots to the top of plants takes place *via* osmosis.
   (iii) Flow of water to various parts of plants is due to osmosis.

Reverse Osmosis and Water Purification

Reverse osmosis occur when the applied external pressure is greater than the osmotic pressure and solvent flows in a reverse way i.e. from higher concentration to the lower concentration.

Water purification is done with the help of reverse osmosis and pure water is obtained.

In regions, where there is lack of freshwater, but sea water is easily available, desalination of sea water is done with the help of reverse osmosis on a large scale basis and pure water is obtained.

This process requires less energy than the process of distillation and hence more efficient.

Abnormal Colligative Properties (van't Hoff Factor)

Since, colligative properties depend upon the total number of particles of solute. Therefore, any change in the number of particles of solute leads to a change in colligative properties.

1. **In case of dissociation** If 1 molecule of solute A dissociates to yield 'n' ions and α is the degree of dissociation then the total number of moles in solution $= (1-\alpha) + n\alpha = 1 + (n-1)\,\alpha$

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van't Hoff factor,

$i \quad 1 \quad (n \quad 1) \qquad 1$

if $n \quad 2$

and $\dfrac{(i \quad 1)}{(n \quad 1)}$

2. **In case of association** If n molecules associate to form one giant molecule and is the degree of association then the total number of moles in solution

$(1 \qquad) \quad \dfrac{}{n}$

$1 \qquad \dfrac{1}{n} \quad 1$

van't Hoff factor

$1 \qquad \dfrac{1}{n} \quad 1 \qquad 1$

if $n \quad 2$

and $\dfrac{(i \quad 1)}{\dfrac{1}{n} \quad 1}$

van't Hoff factor (i) and its significance

$i \quad \dfrac{\text{Observed value of colligative property}}{\text{Normal value of same property}}$

Formulae Related to Colligative and Abnormal Colligative Properties

Colligative properties

Relative lowering of vapour pressure $\dfrac{p \quad p_s}{p} \quad \dfrac{n}{N} \quad \dfrac{W_{solute}}{W_{solvent}} \quad \dfrac{M_{solvent}}{M_{solute}}$

where, n and N are moles of solute and solvent respectively.

Elevation in boiling point (T_b) $K_b m \quad \dfrac{K_b W_{solute} \quad 1000}{M_{solute} \quad W_{solvent}} \quad \dfrac{MR(T_b)^2}{H_{vap} \quad 1000} \quad \dfrac{0.002T^2}{l_v}$

where, M molar mass of solvent, T_b boiling point of pure solvent

R gas constant, T_b boiling point of solution, K_b molal boiling point elevation constant,
T normal boiling point of pure solvent,
l_v latent heat of evaporation in cal/g of pure solvent.

Depression in freezing point (T_f) $K_f m \quad \dfrac{MR(T_t)^2}{H_{fusion} \quad 1000} \quad \dfrac{0.002(T)^2}{l_f}$

where, T_t freezing point of solvent, T normal freezing point of solvent

l_f latent heat of fusion

Osmotic pressure ( ) $\dfrac{n_{solute} \quad RT}{V_{solute}}$ For mixture of different gases $\quad 1 \quad 2 \quad \ldots$

For isotonic solutions, $\quad 1 \quad 2$

Abnormal colligative properties

van't Hoff factor (i) $\dfrac{\text{Calculated molecular mass } (M_c)}{\text{Observed molecular mass } (M_o)}$

Relative lowering in vapour pressure, $\dfrac{p_A \quad p_A}{p_A} \quad i \quad B$

$T_f \quad iK_f m, \quad T_b \quad iK_b m, \quad \dfrac{in_{solute} \quad RT}{V_{solution}}$

Table showing van't Hoff factor i for different electrolytes

Solute type	Example	Ionisation or association	Number of particles in the solution from 1 mole solute	van't Hoff factor 'i'
Non-electrolyte	Urea, sucrose, glucose		1	1
Binary electrolyte AB type	NaCl, KCl CH_3COOH etc.	$AB \rightleftharpoons A \quad B$ (1)	2	1
Tertiary electrolyte AB_2 type or A_2B type	$CaCl_2$, $BaCl_2$ H_2SO_4, $K_2[PtCl_6]$	$AB_2 \rightleftharpoons A^2 \quad 2B$ (1, 2) $A_2B \rightleftharpoons 2A \quad B^2$ (1, 2)	3 3	$1 \quad 2$ $1 \quad 2$
Quaternary electrolyte AB_3 or A_3B type	$AlCl_3$, $K_3[Fe(CN)_3]$ $FeCl_3$, K_3PO_4	$AB_3 \rightleftharpoons A^3 \quad 3B$ (1, 3) $A_3B \rightleftharpoons 3A \quad B^3$ (1, 3)	4 4	$1 \quad 3$ $1 \quad 3$
Association of solute	Benzoic acid forming dimer in benzene	$nA \rightleftharpoons An$ (1, $\frac{}{2}$)	$\frac{1}{n}$	$1 \quad 1 \quad \frac{1}{n}$
General electrolyte $AB_{n \quad 1}$	One mole of solute giving n ions in the solution	$AB_{n \quad 1} \rightleftharpoons A^{(n \quad 1)} \quad (n \quad 1)B$ (1, $(n \quad 1)$)	n	$[1 \quad (n \quad 1) \quad]$

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Best Practice SHOTS

22. The elevation in boiling point of a solution of 13.44 g of $CuCl_2$ in 1 kg of water using the following information will be (molecular weight of $CuCl_2$ = 134.4 $gmol^{-1}$ and $K_b = 0.52\ K\ molal^{-1}$)
(a) 0.16 *(b)* 0.05 *(c)* 0.1 *(d)* 0.2

23. Osmotic pressure measurement is useful particularly for biomolecules which are generally unstable
(a) at lower temperature *(b)* at higher pressure
(c) at lower pressure *(d)* at higher pressure

24. A certain substance A tetramerises in water to the extent of 80%. A solution of 2.5 g of A in 100 g of water lowers the freezing point by 0.3°C. The molar mass of A is
(a) 31 *(b)* 62 *(c)* 122 *(d)* 244

25. Molecules of acetic acid dimerise in benzene due to hydrogen bonding. It happens in solvents having
(a) high dielectric constant *(b)* low dielectric constant
(c) high concentration *(d)* normal colligative property

26. Chemical potential of a species in an ideal solution is lower than the chemical potential of pure component. It is due to
(a) colligative properties *(b)* ebullioscopy
(c) osmosis *(d)* azeotropic

27. Different movements of plants such as opening and closing of flowers, etc., are controlled by
(a) osmosis *(b)* dissociation
(c) van't Hoff factor *(d)* colligative property

28. Semipermeable membrane can be
(a) animal or vegetable origin *(b)* pigs bladder or parachment
(c) cellophane *(d)* All of these

29. Assuming each salt to be 90% dissociated which of the following will have highest osmotic pressure?
(a) Decinormal $Al_2(SO_4)_3$
(b) Decinormal $BaCl_2$
(c) Decinormal Na_2SO_4
(d) A solution obtained by mixing equal volumes of *(b)* and *(c)* and filtering

30. $PtCl_4 \times 6H_2O$ can exist as a hydrated complex 1 m aqueous solution has the depression in freezing point of 3.72 : Assume 100% ionisation and $K_f(H_2O) = 1.86°\ mol^{-1}kg$, then the complex is
(a) $[Pt(H_2O)_6]\ Cl_4$ *(b)* $[Pt(H_2O)_4Cl_2]\ Cl_2 \cdot 2H_2O$
(c) $[Pt(H_2O_3)Cl_3]\ Cl \times 3H_2O$ *(d)* $[Pt(H_2O)_2Cl_4]$

31. The freezing point of 0.20 M solution of weak acid HA is 272.5 K. The molality of the solution is 0.263 mol kg^{-1}. The pH of the solution on adding 0.25 M sodium acetate solution will be
(a) 4.11 *(b)* 6.2 *(c)* 5.4 *(d)* 2.2

32. Dry air was successively passed through a solution of 5g solute in 80g water and then through pure water. The loss in the weight of solution was 2.5 g and that of pure water was 0.04 g. The molecular weight of the solute is
(a) 30.31 *(b)* 80.21
(c) 60.51 *(d)* 70.32

33. Which has the maximum osmotic pressure at temperature T ?
(a) 100 mL of 1 M urea solution
(b) 300 mL of 1 M glucose solution
(c) Mixture of 100 mL of 1 M urea solution and 300 mL of 1 M glucose solution
(d) All the above are isotonic

34. If sodium sulphate is considered to be completely dissociated into cation and anion in aqueous solution the change in freezing point of water (ΔT_f), when 0.01 mole sodium sulphate is dissolved in 1 kg of water, is ($K_f = 1.80\ kg\ mol^{-1}$)
(a) 0.0372 K *(b)* 0.0558 K
(c) 0.0744 K *(d)* 0.0180 K

35. The molar mass of a solute X in g mol^{-1}, if its 1% solution is isotonic with a 5% solution of cane sugar (molar mass = 342 g mol^{-1}) is
(a) 68.4 *(b)* 34.2 *(c)* 136.2 *(d)* 171.2

36. Two aqueous solution contain, 7 g urea (molar mass = 60 g) and 42 g of substance X in 100 g of water respectively, freeze at the same temperature. The molecular weight of X is
(a) 460 *(b)* 370
(c) 120 *(d)* 360

37. Which of the following physical properties is used to determine the molar mass of a polymer solution?
(a) Relative lowering of vapour pressure
(b) Elevation in boiling points
(c) Depression in freezing point
(d) Osmotic pressure

Answers

1. (a)	**2.** (a)	**3.** (a)	**4.** (c)	**5.** (c)	**6.** (a)	**7.** (d)	**8.** (b)	**9.** (c)	**10.** (b)
11. (a)	**12.** (b)	**13.** (c)	**14.** (c)	**15.** (b)	**16.** (c)	**17.** (b)	**18.** (d)	**19.** (a)	**20.** (a)
21. (d)	**22.** (a)	**23.** (d)	**24.** (b)	**25.** (b)	**26.** (a)	**27.** (a)	**28.** (d)	**29.** (a)	**30.** (c)
31. (a)	**32.** (d)	**33.** (d)	**34.** (b)	**35.** (a)	**36.** (d)	**37.** (a)			

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MASTER STROKES

1. X_1 and X_2 are the mole fractions of components 1 and 2 respectively in A ..... phase than by using B ..... law of partial pressure $p_1 = y_1\ p_{total}$ and $p_1 = y_2\ p_{total}$. Identify (*A*) and (*B*) in order to complete the above statement.

(a) $A \rightarrow$ liquid; $B \rightarrow$ Dalton
(b) $A \rightarrow$ vapour; $B \rightarrow$ Dalton
(c) $A \rightarrow$ vapour; $B \rightarrow$ Henry
(d) $A \rightarrow$ liquid ; $B \rightarrow$ Henry

Hint y_1 and y_2 are the mole fractions of components 1 and 2 respectively in the vapour phase then using, Dalton's law of partial pressure $p_1 = y_1\ p_{total}$; $p_2 = y_2\ p_{total}$

2. Pure benzene freezes at 5.4°C. A solution of 0.223 g of phenyl acetic acid ($C_6H_5CH_2COOH$) in 4.4g of benzene ($K_f = 5.12$ K kg mol^{-1}) freezes at 4.47°C. By this observation, one can conclude that

(a) phenyl acetic acid exists in benzene
(b) phenyl acetic acid undergoes partial ionisation in benzene
(c) phenyl acetic acid undergoes complete ionisation in benzene
(d) phenyl acetic acid dimerizes in benzene

3. The molar mass of a solute from the osmotic pressure which it produce when a mass *m* of solute is dissolved in volume *V* is given by the expression

(a) $M = \left(\frac{m}{V}\right)\frac{RT}{\pi}$ *(b)* $M = \left(\frac{m}{V}\right)\frac{\pi}{RT}$

(c) $M = \left(\frac{M}{V}\right)\pi RT$ *(d)* $M = \left(\frac{m}{V}\right)\frac{\pi R}{T}$

4. Consider the separate solution of 0.500 M. $C_2H_5OH\ (aq)$, 0.100 M $Mg_3(PO_4)_2\ (aq)$, 0.250 M KBr (aq) and 0.125 M $Na_3PO_4\ (aq)$ at 25°C. Which statement is true about these solutions, assuming all salts to be strong electrolytes?

(a) All of these have the same osmotic pressure
(b) 0.100 M $Mg_3(PO_4)_2\ (aq)$ has the highest osmotic pressure
(c) 0.125 M $Na_3(PO_4)_2\ (aq)$ has the highest osmotic pressure
(d) 0.500 M $C_2H_5OH\ (aq)$ has the highest osmotic pressure

5. Consider the following statements,

I. For same solution $\Delta T_b = \Delta T_f$.
II. 5% solution of urea will have more osmotic pressure than that 10% solution of glucose
III. Elevation of boiling point occurs due to increase in vapour pressure of solution on adding solute.
IV. The depression of freezing point is due to decrease in vapour pressure of solution on adding solute.

Among the above statements.

(a) II and IV are true *(b)* I, II and IV are true
(c) II and III are false *(d)* Only IV is true

6. An organic liquid (*P*) is immiscible with water when boiled with water, the boiling point is 90°C at which the partial pressure of water is 526 mm Hg. The weight ratio of the liquid (*P*) and water collected is 2.5:1. The molecular weight of the liquid (*P*) is

(a) 112.7g mol^{-1} *(b)* 320.8g mol^{-1}
(c) 220.3 g mol^{-1} *(d)* 170.7g mol^{-1}

7. Which is correct order for the molal elevation constant (K_b) values of the following alcohols?

I. $(CH_3)_3C{-}OH$ II. $(CH_3)_2CH{-}CH_2OH$
III. $CH_3CH_2CH_2CH_2OH$

(a) III > II > I *(b)* II > III > I
(c) I > III > II *(d)* II > I > III

8. When a compound $C_{38}H_{30}$ dissolved in benzene, it partially dissociates as in the following reaction,

$C_{38}H_{30} \rightleftharpoons 2C_{19}H_{15}$. If 25.6g of $C_{38}H_{30}$ is dissolved in 400 g of benzene, the freezing point is lowered by 0.680°C. What percentage of $C_{38}H_{38}$ molecules have dissociated? ($K_f = 4.9$)

(a) 5.38% *(b)* 7.01%
(c) 6.20% *(d)* 3.00%

9. 75.2 g of C_6H_5OH (phenol) is dissolved in a solvent of $k_f = 14$. If the depression in freezing point is 7K, then find the percentage of phenol that dimerises.

(a) 20% *(b)* 30%
(c) 70% *(d)* 90%

10. When 25g of a non-volatile solute is dissolved in 100 g of water, the vapour pressure is lowered by 2.25×10^{-1} mm Hg. If the vapour pressure of water at 20°C is 17.5 mm Hg. What is the molecular weight of the solute?

(a) 206 *(b)* 302 *(c)* 350 *(d)* 276

11. 100 cc of 1.5% solution of urea is found to have an osmotic pressure of 6.0 atm and 100cc of 3.42% solution of cane sugar is found to have an osmotic pressure of 2.4 atm. If the two solutions are mixed, the osmotic pressure of the resulting solution will be

(a) 8.4 atm *(b)* 4.2 atm *(c)* 16.8 atm *(d)* 2.1 atm

12. Which of the following statement is not correct?

(a) Molarity of a solution in liquid state changes with temperature
(b) ΔH_{mix} and ΔV_{mix} for an ideal solution is zero
(c) The lowering of vapour pressure of a solution causes depression in the freezing point
(d) The extent of dissociation decreases steadily with increasing dilution

Answers

1. (b) **2.** (d) **3.** (a) **4.** (a) **5.** (d) **6.** (a) **7.** (a) **8.** (a) **9.** (c) **10.** (c)
11. (b) **12.** (d)

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Questions to Measure Your Problem Solving Skills

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7. *Use log tables if necessary, use of calculator is not allowed.*

1 Very Short Answer Type Questions (1 Mark)

1. Give the IUPAC name of glycerol.

Hint Propane - 1, 2, 3 - trial.

2. Give an example of thermosetting polymer.

Hint They have cross-linked structures.

3. Define the term chemotherapy.

Hint Treatment of diseases.

4. Give two examples of tranquilisers.

Hint These release mental anxieties.

5. Rearrange the following in an increasing order of their basic strength.

$C_6H_5NH_2$, $C_6H_5N(CH_3)_2$, $(C_2H_5)_2NH$ and CH_3NH_2

Hint $C_6H_5NH_2$ $C_6H_5N(CH_3)_2$ CH_3NH_2 $(C_2H_5)_2NH$

2 Short Answer Type Questions (2 Marks)

6. Using IUPAC norms write the formulae for the following coordination compounds:

(i) Hexaamminecobalt (III) chloride

(ii) Potassium tetrachloridonickelate (II)

Hint (i) $[Co(NH_3)_6]Cl_3$ (ii) $K_2[NiCl_4]$

7. Out of *o*-nitrophenol and *o*-cresol, which is more acidic?

Hint *o*-nitrophenol is more acidic due to electron withdrawing nature of NO_2 group.

8. Illustrate the following name reactions giving suitable example in each case.

(i) Clemmensen reduction

(ii) Hell-Volhard-Zelinsky reaction

or

How are the following conversions carried out?

(i) Acetic acid to methylamine

(ii) Acetaldehyde to methane

Hint (i)

$$CH_3COOH \xrightarrow{NH_3} CH_3COONH_4 \xrightarrow[H_2O]{} CH_3CONH_2 \xrightarrow{NaOBr} \underset{\text{Methylamine}}{CH_3NH_2}$$

(ii) $$CH_3CHO \xrightarrow[CrO_3]{[O]} CH_3COOH \xrightarrow{NaOH} CH_3COONa \xrightarrow{\text{Sodalime /}} \underset{\text{Methane}}{CH_4}$$

9. Aniline dissolves in *aq*. HCl. Why?

Hint Formation of water soluble salt.

10. Why NaCl crystals when heated in sodium vapours become yellow?

Hint Metal excess defect.

3 Short Answer Type Questions (3 Marks)

11. Nitric acid forms an oxide of nitrogen on reaction with P_4O_{10}. Write the reaction involved and draw the resonating structures of oxide of nitrogen formed.

Hint P_4O_{10} acts as a dehydrating agent.

12. Discuss the effect of pressure and temperature on the adsorption of gases on solids.

Hint Effect of pressure-Freundlich isotherm; effect of temperature-Le-Chatelier's principle.

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13. The cell in which the following reaction occurs,
$2Fe^{3+}(aq) + 2I^{-}(aq) \rightarrow 2Fe^{2+}(aq) + 2I_2(s)$
has E_{cell} 0.236 V at 298K. Calculate the standard Gibbs energy and equilibrium constant of the cell reaction.

Hint Standard Gibbs energy, $_rG$ nFE_{cell}
where, n number of electrons taking part in the reaction.
Equilibrium constant is given as, $\log K_c = \frac{G}{2.303\,RT}$

14. 15.0 g of unknown molecular material is dissolved in 450g of water. The resulting solution freezes at 0.34 C. Calculate the molar mass of the material.

Hint T_f $\frac{K_f \; w_2 \; 1000}{M_2 \; w_1}$

15. The half-life for decay of radioactive ^{14}C is 5730 yr. An archaeological artifact containing wood had only 80% of the ^{14}C found in a living tree. Estimate the age of the sample.

Hint First order reaction k $\frac{2.303}{t}\log\frac{[A]_0}{[A]}$; k $\frac{0.693}{t_{1/2}}$

16. Colloidal solution (or sols) are prepared by Bredig's electrical disintegration method. Write the mechanism of this method.

Hint In Bredig's electrical method, electric current is passed through electrodes made of a metal whose solution is to be prepared.

17. How can reducing and non-reducing sugars be distinguished? Mention the structural feature characterising reducing sugars.

18. The treatment of alkyl chlorides with *aq.* KOH leads to the formation of alcohols but in the presence of alc. KOH, alkenes are major products. Explain.

Hint —OH is a good nucleophile while $C_2H_5O^-$ is a strong base.

19. Give reasons for the following.
(i) Formic acid is stronger acid than acetic acid.
(ii) Out of primary, secondary and tertiary alcohols, primary alcohol is the strongest acid.
(iii) *o*-hydroxy benzoic acid (salicylic acid) is stronger acid than *p*-hydroxy benzoic acid.

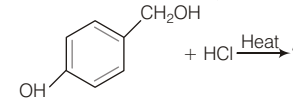
Hint
(i) Greater the stability of carboxylate ion, greater will be the strength of carboxylic acid.
(ii) As an acid, an alcohol dissociates into an alkoxide ion and hydrogen ion, $R{-}OH \rightleftharpoons R{-}O^- + H^+$.
(iii) Anion from salicylic acid is stabilised by intramolecular hydrogen bonding which does not exist in *p*-isomer.

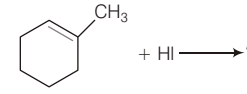
20. Write down the following reactions.
(i) Reaction of aldehydes or ketones with PCl_5.
(ii) Reaction of formaldehyde with ammonia.
(iii) Reaction of chlorobenzene with NaOH at 623 K and 320 atmospheric pressure.

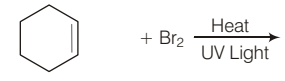
Hint
(i) Aldehydes or ketones reacts with PCl_5, form gem-dihalides.
(ii) Formaldehyde reacts with ammonia to form hexamethylene tetramine $(CH_2)_6N_4$, which is known as urotropine.
(iii) Phenol is obtained.

or

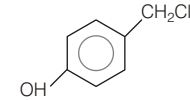
Draw the structure of major monohalo products in each of the following reactions :

(i) 

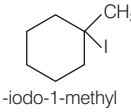
(ii) 

(iii) 

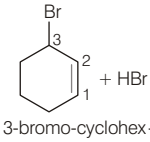
Hint

(i) 

4-chloromethyl phenol

(ii) 

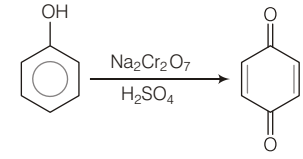
1-iodo-1-methyl cyclohexane (by Markownikov's rule)

(iii) 

3-bromo-cyclohex-1-ene

21. Write the mechanism of the following conversions.
(i) Benzoquinone from phenol.
(ii) Propan-2-ol from propene.
(iii) 2-methylpropan-2-ol from methyl magnesium bromide.

Hint

(i) 

(ii) $CH_3{-}CH{=}CH_2 \xrightarrow{H_2O,\,H^+} CH_3{-}\underset{\underset{\text{Propan-2-ol}}{OH}}{CH}{-}CH_3$

(iii) $CH_3MgBr \xrightarrow[H_2O/H^+]{CH_3COCH_3} CH_3{-}\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}{-}CH_3$

22. Define the following.
(i) Orlon (ii) Antibiotics (iii) Analgesics

4 Value Based Type Question (4 Marks)

23. Trichloromethane or chloroform is a colourless oily liquid with a peculiar smell. It is sparingly soluble in water. The vapour when enhaled cause unconsciousness and therefore, it is used as an anaesthetic.
(i) What happens when chloroform is not protected from oxygen during its storage?
(ii) Why the use of chloroform has been reduced as an anaesthetic now a days.

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Hint
(i) Chloroform is oxidised to poisonous gas phosgene.
(ii) Chronic chloroform exposure may damage liver and kidneys because chloroform is metabolished to poisonous phosgene.

❺ Long Answer Type Questions (5 Marks)

24. Explain the following.

(i) The conductivity of a solution decreases with dilution.

Hint Conductivity number of ions per unit volume.

(ii) Soaps cannot be used in acidic medium.

Hint In acidic medium, the acids present in solution, precipitate the insoluble free fatty acids.

(iii) Carbohydrates are generally optically active.

Hint Because they have one or more chiral carbon atoms.

(iv) Graphite can be used as an anode but not diamond.

Hint Graphite is a good conductor of electricity.

(v) The boiling points of ethers are much lower than those of the alcohols of comparable molar masses?

Hint Alcohols show hydrogen bonding.

or

An organic compound *A* contains 69.77% carbon, 11.63% hydrogen and rest oxygen. The molecular mass of the compound is 86. It does not reduce Tollen's reagent but forms an addition compound with sodium hydrogen sulphite and gives positive iodoform test. On vigorous oxidation, it gives ethanoic and propanoic acids. Derive the structure of compound *A*.

Hint Since, *A* does not give Tollen's test but gives positive iodoform test, hence it is a methyl ketone. Since, on oxidation, it gives ethanoic acid and propanoic acid hence, it is pentan-2-one.

25. (i) Explain the reason.

(a) When ammonia is obtained by Haber's process, it is necessary to remove CO.

(b) Initially hydrolysis of ester is slow and after sometimes, it become faster.

Hint
(a) CO acts as a poison for catalyst used in the manufacture of ammonia.
(b) Acid produced in the reaction acts as auto catalyst.

(ii) Nickel does not form low spin octahedral complexes.

Hint For octahedral complexes, coordination number should be 6. Ni has only one empty *d*-orbital, so it can only form high spin octahedral complexes.

(iii) What is meant by stability of a coordination compound in solution?

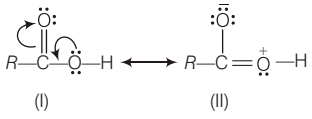
Hint Degree of association between the two species is involved in the state of equilibrium.

(iv) What are expected products of hydrolysis of lactose? Give reaction.

Hint Lactose is a disaccharide of glucose and galactose.

(v) Draw the resonating structure of *R*COOH.

Hint



(I) (II)
(Charge-separated structure)

or

(i) Give the IUPAC name, electronic configuration, coordination number and oxidation state of the following complexes.

(a) $K[Cr(H_2O)_2(C_2O_4)_2]\ 3H_2O$
(b) $[Co(NH_3)_5Cl]Cl_2$ (c) $CrCl_3(Py)_3$
(d) $Cs[FeCl_4]$

(ii) Write the two basic requirements for refining a metal by Mond's process.

Hint $Ni + 4CO \rightleftharpoons Ni(CO)_4$ (450 – 470 K) $Ni + 4CO$

26. (i) What is effective nuclear charge (Z_{eff})?

(ii) How do we calculate the depression in freezing points (T_f) ?

Hint T_f $K_b m$

(iii) Write the important factors which affect the rate of reactions ?

Hint Keywords : conc. of reactants, temperature, catalyst.

(iv) Give the Pictorial representation of electrodialysis.

Hint **Principle** Particles of crystalloids pass through animal membrane whereas those of colloids do not.

Application Purification of blood in artificial kidney.

(v) Distinguish between

Hint Cyclopentanol dissolves in conc. H_2SO_4 while cyclopentylchloride does not dissolve in conc. H_2SO_4 and two distinct layers are formed.

or

(i) What is the role of collectors in froth floatation process?

Hint Enhance non-wettability of the mineral particles.

(ii) Why is the bond angle in PH_3 is lesser than that in NH_3 molecule?

Hint On moving down the group, size of the central atom increases and electronegativity decreases. Due to this, repulsion between bond pair of electrons decreases.

(iii) Draw the structure of XeO_3 .

(iv) Why Cd^{2+} salts are white?

Hint Because Cd^{2+} has completely filled *d*-orbitals (d^{10}).

(v) Complete the following reaction :

$$CH_3CH_2CH=CH_2 \quad HBr$$

Hint $CH_3-CH_2-\underset{\displaystyle Br}{\underset{|}{CH}}-CH_3$

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❶ Very Short Answer Type Questions (1 Mark)

1. Give one example each of stabiliser and depressant used in froth floatation process.

Hint Stabiliser - aniline

Depressant - NaCN in case of ores of ZnS and PbS.

2. A solution of KOH hydrolysis $CH_3CHClCH_2CH_3$ and $CH_3CH_2CH_2CH_2Cl$. Which one of these is more easily hydrolysed?

Hint 2° halide will be hydrolysed more easily.

3. Schottky defect lowers the density of related solids. Explain.

Hint Equal number of cations and anions are missing from the lattice (vacancy defect).

4. Write the dispersed phase and dispersion medium of butter.

Hint Dispersed phase-liquid, dispersion medium-solid.

5. Calculate the molarity of 30 g of $Co(NO_3)_2 \times 6H_2O$ in 4.3 L of solution. (Atomic mass of Co = 59)

Hint $\text{Molarity} = \frac{w_2}{M_2} \times \frac{1}{\text{volume (L)}} = 0.024\ \text{M}$

❷ Short Answer Type Questions (2 Marks)

6. (a) How many unpaired electrons are present in a substance having magnetic moment of 3.9 BM?

(b) Why is the separation of lanthanoid elements difficult?

Hint (a) $\mu = \sqrt{n(n+2)} \Rightarrow n = 3$

(b) Due to lanthanoid contraction, difference in size of metal atoms or ions is very small.

7. Convert

(a) 3-methylaniline to 3-nitrotoluene

(b) Aniline to 1,3,5 - tribromobenzene.

Hint (a) *Step* 1 Diazotisation, Step 2 Oxidation ($NaNO_2/Cu/\Delta$)

(b) *Step* 1 Bromination, *Step* 2: Diazotisation, *Step* 3, Reduction by $Cu / H_3PO_3 / H_2O$.

8. By how much times will the rate of a reaction increases in the presence of catalyst, if activation energy of a reaction is lowered by 2 kcal at 27°C?

or

Find the half-life of the first order reaction, if the rate is 0.04 mol $L^{-1}s^{-1}$ at 10 min and 0.03 mol $L^{-1}s^{-1}$ at 20 min, after initiation.

Hint $\log k = \log A - \frac{E_a}{2.303RT}$; $\log k' = \log A - \frac{E_a - 2}{2.303RT}$

$\Rightarrow k' = 28k$ or $k = \frac{2.303}{t_2 - t_1} \log \frac{[A]_1}{[A]_2}$, $\frac{(\text{rate})_1}{(\text{rate})_2} = \frac{[A]_1}{[A]_2}$

$t_{1/2} = \frac{0.693}{k} \Rightarrow t_{1/2} = 1457.9\ \text{s}$

9. What do you understand by stepwise stability constant and overall stability constant of a coordination compound? How are these two constants related?

10. How is shape-selective catalysis used in obtaining gasoline from alcohol? Name the catalyst used in this process.

Hint The catalyst used is zeolite catalyst (ZSM - 5).

It converts alcohols directly into gasoline by dehydrating them to give a mixture of hydrocarbons.

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❸ Short Answer Type Questions (3 Marks)

11. (a) Why are splitting patterns of *d*-orbitals in octahedral and tetrahedral geometry reverse of each other?

(b) Write the electronic configuration of d^5 species in an octahedral field when

(i) $\Delta_o > p$ (ii) $\Delta_o < p$

in terms of t_{2g} and e_g *d*-orbitals.

Hint (a) In octahedral complexes - axial orbitals repelled. In tetrahedral complexes-non-axial orbitals are repelled.

(b) (i) $t_{2g}^5 e_g^0$ (Strong field ligands, pairing occurs low spin complexes).

(ii) $t_{2g}^3 e_g^2$ (Weak field ligands, no pairing, high spin complexes).

12. Give reasons for the following.

(i) Alumina is dissolved in cryolite instead of being electrolysed directly.

(ii) Zinc oxide can be reduced to the metal by heating with carbon but not Cr_2O_3.

(iii) Extraction of copper directly from sulphide ores is less favourable than that from its oxide ore through reduction.

Hint (i) Cryolite lowers the melting point of alumina.

(ii) The free energy change for the formation of Cr_2O_3 is more negative than that of ZnO.

(iii) The standard free energy for the formation of CS_2 is less negative than that of CO_2 and CO.

13. Account for the following.

(i) The enthalpies of atomisation of the transition metals are high.

(ii) The lowest oxide of a transition metal is basic, the highest is amphoteric/stane acidic.

(iii) Cobalt (II) is stable in aqueous solution but in presence of complexing agents, it is easily oxidised.

Hint (i) Due to strong metallic bonding and additional covalent bonding.

(ii) In lower oxidation states, transition metals behave like metals and metal oxides are basic in nature. As the oxidation state increases, its metallic character decreases due to decrease in size, thus it becomes less metallic. Thus, in higher oxidation state, transition metal oxides are amphoteric or acidic.

14. (a) If three elements *A*, *B* and *C* crystallise as follows : *A*-atoms at the corners, *B*-atoms at centres of cube, *C*-atoms at face centres of cube,

What is the formula of the compound?

(b) A rock salt structure of iron atoms is formed with its effective atomic radius as 1.42 Å. Calculate its density (Molar mass of Fe = 56 u).

Hint (a) ABC_3 (b) Density, $d = \frac{Z \times M}{a^3 \times N_0} = 5.74\ g/cm^3$

15. Consider 19.5 g of CH_2FCOOH to be dissolved in 500g of water. The depression in freezing point of water observed is 1.0°C. Calculate the van't Hoff factor and dissociation constant of fluoroacetic acid.

Hint van't Hoff factor, *i*

$$= \frac{(M_2)_{cal}}{(M_2)_{obs}} = \frac{(12+2+19+12+16+16+1)}{\left(\frac{K_f \times w_2 \times 1000}{\Delta T_f \times w_1}\right)} = 1.0753$$

$$\alpha = i - 1 = 0.0753; C = \frac{w_2/M_2}{V} = 0.5M$$

$$K_a = \frac{[CH_2FCOO^-][H^+]}{[CH_2FCOOH]} = \frac{C\alpha^2}{1-\alpha} = 3.07 \times 10^{-3}$$

16. The decomposition of phosphine PH_3, proceeds according to the following equation,

$$4PH_3(g) \rightarrow P_4(g) + 6H_2(g)$$

It is found that the reaction follows the following rate equation: Rate = $k[PH_3]$. The half-life of PH_3 is 37.9 s at 120°C.

(a) How much time is required for 3/4th of PH_3 to decompose?

(b) What fraction of the original sample of PH_3 will remain behind after 1 min?

Hint (a) Half-life, $t_{1/2} = \frac{0.693}{k} \Rightarrow k = 0.0183\ s^{-1}$

For first order reaction,

$$t = \frac{2.303}{k} \log \frac{[A]_0}{[A]} = 75.84\ s$$

(b) $k = \frac{2.303}{t} \log \frac{[A]_0}{[A]}$ (After 1 min)

$\frac{[A]}{[A]_0} \simeq \frac{1}{3} \Rightarrow$ 33% of PH_3 is remaining fraction.

17. Give reasons.

(a) pK_b value for aniline is more than that for methyl amine.

(b) Electrophilic substitution in benzoic acid takes place at *meta*-position.

(c) The treatment of alkyl chloride with aqueous KOH leads to the formation of alcohol but in the presence of alcoholic KOH, alkene is the major product.

Hint (a) Aniline is weaker base than methylamine due to delocalisation of its lone pair of nitrogen atom in benzene ring.

(b) –COOH group shows electron withdrawing nature.

(c) Aqueous KOH is almost completely ionised to give $\bar{O}H$ ions which being strong nucleophile gives a substitution reaction. But an alc. KOH solution contains alkoxide *RO* ions which being much stronger base than $\bar{O}H$ ions. Hence $R\bar{O}$, preferentially eliminates a molecule of HCl from an alkyl chloride to form alkenes.

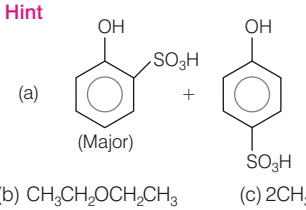
18. Complete the following reactions:

(a) Phenol + H_2SO_4 (conc.) $\xrightarrow{25^\circ C}$

(b) $2CH_3CH_2OH \xrightarrow[413\ K]{96\%\ H_2SO_4}$

(c) $CH_3OCH_3 + \underset{(Excess)}{HI} \rightarrow$

Hint

(a) 

(b) $CH_3CH_2OCH_2CH_3$ (c) $2CH_3I$

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19. How can we distinguish between the following pairs of compounds?

(a) Benzoic acid and ethyl benzoate

(b) Phenol and benzoic acid

(c) Acetophenone and benzophenone

Hint (a) **Sodium bicarbonate test** CO_2 gas evolved in case of benzoic acid only.

(b) **$FeCl_3$ test** Phenol gives violet colouration while benzoic acid does not give any colour.

(c) **Iodoform test** Yellow precipitate of CHI_3 formed with acetophenone only.

20. Explain the following terms:

(a) Invert sugar (b) Reducing sugar (c) Polypeptides

or

Complete the following reactions.

(a) $Ca_3P_2(s) + H_2O(l) \rightarrow$

(b) $SO_3 + H_2SO_4$ (conc.) $\rightarrow$

(c) $MnO_4^- + NO_2^- + H^+ \rightarrow$

Hint

(a) $Ca_3P_2(aq) + 6H_2O(l) \rightarrow 3Ca(OH)_2(aq) + 2PH_3(g)$

(b) $SO_3 + H_2SO_4$ (conc.) $\xrightarrow{\text{Oleum}} H_2S_2O_7$

(c) $2MnO_4^- + 5NO_2^- + 6H^+ \rightarrow 2Mn^{2+} + 5NO_3^- + 3H_2O$

21. Write chemical equations for the synthesis of

(i) Terylene (ii) Neoprene

(iii) Teflon

22. Discuss the role of colloids in the following natural phenomena.

(a) Blue colour of sky (b) Formation of fog

(c) Formation of delta

4 Value Based Type Question (4 Marks)

23. A neuro-patient was prescribed by a neuro-specialist with some antibiotics and vitamin-B complex supplement for a period of three years. The patient used to skip the supplement considering as an extra medicine but used to take the antibiotics regularly with good and well nourished vegetarian diet. After three years, he started feeling symptoms like tingling sensation in fingers, fatigue, nervousness and numbness.

(a) Why vitamin-B complex supplement was advised by the doctor with antibiotics?

(b) Which vitamin deficiency causes such symptoms?

(c) Why did he suffered from that vitamin deficiency although he used to take good and well-nourishing vegetarian diet?

(d) What values are possessed by doctor and patient?

Hint (a) Antibiotics lowers the level of vitamin-B in the body.

(b) Vitamin B_{12}

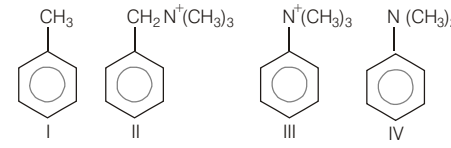
(c) Vitamin-B_{12} is found mostly in animal foods like fish, liver, kidney, eggs, beff, pork etc.

(d) **Values possessed by doctor** Intellectual knowledge, human concern, dedication to his work.

Values possesed by patient Overconfidence over his knowledge, disrespect towards a doctor's advice.

5 Long Answer Type Questions (5 Marks)

24. (a) Arrange the followings in the increasing order of reactive towards electrophilic substitution :



(b) Give a chemical test to distinguish between

(i) Methylamine and dimethylamine

(ii) aniline and N-methyl amine or

(a) Giving an example for each, describe the following reactions.

(i) Hofmann bromamide reaction

(ii) Gattermann reaction

(iii) Coupling reaction

(b) (i) Write the IUPAC name of

$$CH_3 - C \equiv C - CH = CH - C(=O) - OH$$

(ii) Carboxylic acids have higher boiling points than alcohols of comparable molecular masses.

Hint (a) Order of S_E : III < II < I < II Reactivity increases with increase in electron density in benzene ring.

(b) Carbylamine test or

(b) (i) Hex-2-en-4-yn-1-oic acid

(ii) Since, –OH group in carboxylic acids is strongly polarised due to carboxyl group and O of carboxyl group also participate in H-bonding.

25. (a) If measured resistance of decinormal solution of NH_4OH is 1607.72 Ω, find the molar conductivity of this solution.
(Cell constant = 1.5 cm^{-1}).

(b) The molar conductivities at infinite dilution of NH_4Cl, NaOH and NaCl are 129.8 S cm^2 mol^{-1}, 217.4 S cm^2 mol^{-1} and 108.9 S cm^2 mol^{-1}, respectively at 291 K. Calculate percentage dissociation and dissociation constant of NH_4OH solution. or

(a) What will be the thickness of silver deposited on a metallic vessel of surface area 800 cm^2 by passing a current 0.2 A for 3 h? $\rho_{Ag} = 10.74\ g/cm^3$; Atomic mass of Ag = 107.92u)

(b) A voltaic cell is set up at 25°C with half-cells

$Al / Al^{3+}(0.001M)$; $E^\circ_{Al^{3+}/Al} = -1.66$ V

$Ni / Ni^{2+}(0.50M)$; $E^\circ_{Ni^{2+}/Ni} = -0.25$ V

Construct the cell and determine the cell potential.

Hint (a) Molar conductivity, $\Lambda_m = \frac{\kappa \times 1000}{\text{Molarity}} = 9.33$

(b) $\Lambda^\circ_m(NH_4OH) = \Lambda^\circ_m(NH_4Cl) + \Lambda^\circ_m(NaOH) - \Lambda^\circ_m(NaCl)$

$\alpha = \frac{\Lambda_m}{\Lambda^\circ_m} = 0.0392$ ⇒ % Dissociation = 3.92%

$K_a = \frac{C\alpha^2}{1-\alpha}$, ($\because C = 0.1$ M) ⇒ $K_a = 1.599 \times 10^{-5}$

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or

(a) *Step* I : Total charge, $Q = It = 2160\,C$

Step II : Amount of Ag deposited $= \frac{Q \times M}{F} = 2.415g$

Step III : Volume deposited $= \frac{\text{Mass}}{\text{Density}} = 0.2307\ cm^3$

Step IV :

Thickness deposited $= \frac{\text{Volume}}{\text{Area}} = 2.88 \times 10^{-4}$ cm

(b) $E°_{cell} = E°_{cathode} - E°_{anode} = 1.41\ V$

$E_{cell} = E°_{cell} - \frac{0.0591}{n} \log \frac{[Al^{3+}]^2}{[Ni^{2+}]^3} = 1.46\ V$

26. (a) Which one of PCl_4^+ and PCl_4^- is not likely to exist and why?

(b) What does happen when dioxygen is subjected to silent electric discharge?

(c) The electron gain enthalpy (EGE) with negative sign for fluorine is less than that for chlorine, still fluorine is a stronger oxidising agent than chlorine.

(d) (i) Draw the structures of XeF_2, XeF_4 and XeF_6.

(ii) Give the reactions of these compounds with water.

or

(a) Why does H_3PO_3 act as a reducing agent but H_3PO_4 does not ?

(b) Draw the structures of (i) H_2SO_3 (ii) $H_2S_2O_8$

(c) Why interhalogen compounds like AB_5, AB_7 are formed by fluorine?

(d) Give two important uses of each (i) neon, (ii) argon.

Hint (a) PCl_4^- due to less stable oxidation state (+3) of P.

(b) $3O_2(g) \xrightarrow{\text{Silent electric discharge}} 2O_3(g);\ \Delta H° = +142\ kJ/mol$

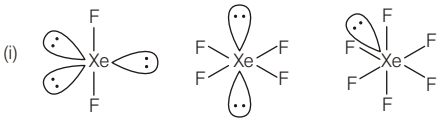
Silent electric discharge prevent decomposition of ozone back to dioxygen.

(c) Bond dissociation enthalpy (BDE) : $F_2 < Cl_2$

Hydration enthalpy (HE) : $F_2 > Cl_2$

Oxidising power depends upon (i) BDE (ii) EGE (iii) HE

(d)

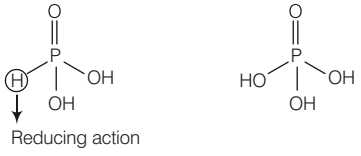
(i) 

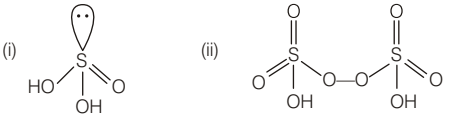
(ii) $2XeF_2 + 2H_2O \rightarrow 4HF + O_2 + 2Xe$

$6XeF_4 + 12H_2O \rightarrow 24HF + 3O_2 + 4Xe + 2XeO_3$

$XeF_6 + 3H_2O \rightarrow 6HF + XeO_3$

or

(a) 

(b) 

(c) Small size and higher electronegativity or oxidising power.

(d) (i) **Neon** For filling sodium vapour lamps.
It is used in safety devices for protecting electrical instruments.

(ii) **Argon** In gas chromatography.
For filling electric bulbs.

Answers of Board Exam Corner (November Issue)

2. $[Pt(NH_3)BrCl(NO_2)]^-$

3. Because of high electronegativity of fluorine and oxygen.

4. $CaCO_3 \xrightarrow{\Delta} CaO + CO_2$

5. Streptokinase

6. Fe^{3+} from rust forms stable soluble complex with chelating oxalate ion furnished by oxalic acid.

7. $2Cu + O_2 + H_2O + CO_2 \rightarrow \underset{\text{Basic copper carbonate (Green)}}{CuCO_3 \cdot Cu(OH)_2}$

8. $\text{Rate} = \frac{-1}{2}\frac{d[A]}{dt} = -\frac{1}{2}\frac{[0.7-0.8]}{[15-0]} = 3.33 \times 10^3\ mol\ L^{-1}\ min^{-1}$

9. $\text{Time} = \frac{\text{Quantity of electricity}}{\text{Current}} = 40.21$ hours

10. $\Delta T_b = \frac{K_b \times 1000 \times w_B}{w_A \times M_B} = 0.052\ K$

11. Radius $(r) = \frac{a}{a\sqrt{2}}$

$D(\text{density}) = \frac{Z \times M}{a^3 \times N_0} = 8.94\ gcm^{-3}$ (N_0 = Avogadro number)

15. (i) The activation energy for combustion reactions of fuels is very high.

(ii) Freezing point of a liquid depresses on the addition of a non-volatile solute whereas boiling point is elevated on the addition of non-volatile solute.

16. $\log k = \log A - \frac{E_a}{2.303RT}$

$\frac{K_2}{K_1} = 2.163 \times 10^4$

19. (i) Nitrogen does not have *d*-orbitals to expand its octet

(ii) Bi has larger size than Sb

20. (i) $2Ag + PCl_5 \rightarrow 2AgCl + PCl_3$

(ii) $Fe_2O_3 + Al(s) \xrightarrow{\Delta} Al_2O_3(s) + 2Fe + \text{Heat}$

(iii) $5C_2O_4^{2-} + 2MnO_4^- + 16H^+ \rightarrow 2Mn^{2+} + 8H_2O + 10CO_2$

or

$\text{Molar mass } (M) = \frac{a^3 \times N_A \times d}{z}$

$= \frac{(300 \times 10^{-10})^3 \times (6.023 \times 10^{23}) \times 6}{4} = 24.39\ gmol^{-1}$

$\text{Radius } (r) = \frac{a}{2\sqrt{2}} = \frac{300}{2\sqrt{2}} = 106.06$ pm

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21. Partial pressure = % of component × total pressure.
According to Henry's law, partial pressure = Henry constant × mole fraction proportion of N_2 and O_2 = 2 : 1

23. (i) Ozone absorbs ultraviolet radiations
(ii) Chlorofluorocarbon and nitric oxide.

24. (i) No, because $E°_{cell} < 0$
(ii) Rate = $k[A]^3$, order = 3
(iv) Because it is always occur due to attraction between adsorbate and adsorbent molecules and hence, energy is always released.
(v) Al is stronger reducing agent than C.

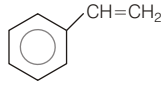
25. (i) Dust particles along with water suspended in air scatter blue light.
(ii) Concentration of reactants keeps on decreasing.
(iii) Magnesium prevents the oxidation of steel by transferring the excess of electrons to the steel.
(iv) Because the number of ions per unit volume furnished by an electrolyte decreases with dilution.
(v) Due to heating during the day and cooling at night over a number of years, glass acquires some crystalline character and hence, looks milky.

26. (i) $\Delta T_f = ik_f m = -1.59°C$

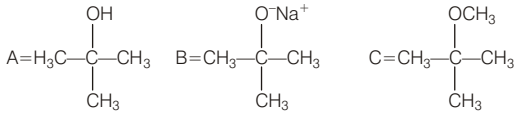
(ii) $\lambda°_{(HCOOH)} = \lambda°_{(H^+)} + \lambda°_{(HCOO^-)}$ $\alpha = \frac{\lambda^m_c}{\lambda^m_o}$; $K_c = \frac{c\alpha}{1-\alpha}$

or $\rightarrow$ Rate = $k\ [A]^p\ [B]^q$ $\rightarrow$ Final rate law expression is
rate = $k[A][B]^2$, $k = 6\ mol^{-2}L^2min^{-1}$

Answers of Board Exam Corner (November Issue)

1.


2. 3-methyl penta-2, 4-diene-1,2-diol
3. Cyanocobalamin.
4. Nylon - 6,6.
5. Phenol.

7.


10. C—I bond is quite weak as compared to C—Cl bond.

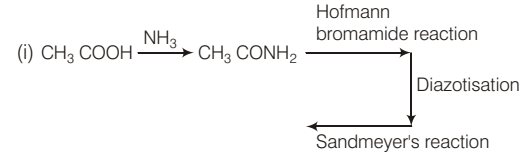
11. (i) 3-bromo-2-methylbut -1-ene
(ii) 2-chloro-2-methylbutane (iii) 2-ethoxy-2-methylpropane

12. (i) Stability of carbonation decides racemisation or inversion.
(ii) For E2-elimination, deprotonating groups should be are anti planar to each other.
(iii) Due to nucleophilic nature of alkyl part of G.R

13. (i) NaOH, 368K, H^+ (ii) Na, ether
(iii) Mg ether, CO_2, H_2O

14. (i) Draw like nucleophilic addition reaction of ketone.
(ii) Formation of cyanohydrin.
(iii) Due to resonance stabilisation.

15. (i) Flow of electron from NH_2 to NO_2 group.
(ii) Flow of electron from OH to *p*-NO_2 group.
(iii) Flow of electron from OMe to conjugated π-bonds.

16. (i)


(ii) This is the process of alkylation at N-atom of amide group.

17. (i) At C-1 same configuration defines anomer.
(ii) Formation of H-bonding explains the solubility in water.
(iii) Enzymes reduces the magnitude of activation energy but does not take part in a chemical reaction.

18. Reduction at carbonyl group results the chiral center in the product which have stereoisomers.

19. (i) Acidic strength $\mu \frac{1}{pK_a}$
(ii) Greater is the delocalisation of lone pair of electrons, lesser will be its basic strength.
(iii) Reactivity of S_N1 reaction α stability of carbocation

21. (i) EWG reduces electron density of that center where it is placed.

23. (i) D : dextrorotatory
(ii) High amount of glucose stops the flows of blood in veins.
(iii) Check out with Fehling solution or Tollen's reagent.
(iv) Kindness, tendency to help the people.

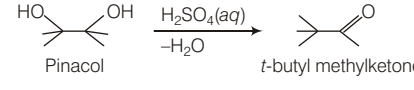
24. (i) Due to partial double bond character produced by —Cl in haloarenes, reduces bond length.
(ii) ¾ OMe provides more electron density through resonance than ¾ Cl
(iii) Due to stability of conjugate base.
(iv) Rate of Solvolysis α Stability of carbonation.
(v) Due to presence of-I effect exhibiting —NO_2 group.

or

(i) Step - 1 : PCC, Step - 2 : MgBr/CuCl
(ii) Step - 1 : Diazotisation reaction
Step - 2 : Ring extension, Step - 3 : Hydrolysis
(iii) MeOH, NaOH / Δ
(iv) Step - 1 : NH_3, Step - 2 : Strong heating

25. (i) Evolution of CO_2.
(ii) N - ethyl benzene sulphonamide.
(iii) isocyanide (iv) A copolymer.

26. (i) The both migrating groups must be placed at the anti periplanar to the each other.



Pinacol *t*-butyl methylketone

(iii) $RCO_2H + HN_3 \rightarrow RNH_2$ or
Compound having —$COCH_3$ group gives haloform test. Alkene undergoes ozonolysis more readily.

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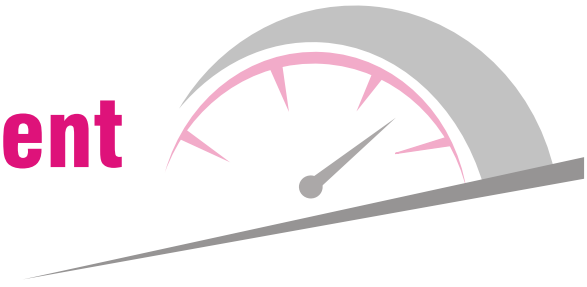
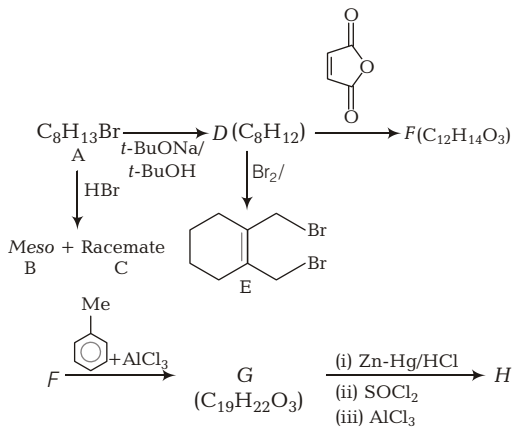
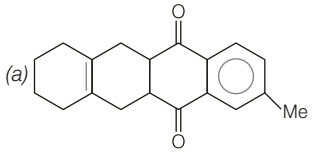
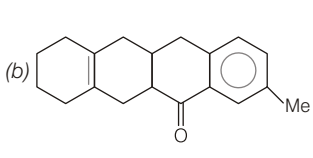
Quizzer (No.14)

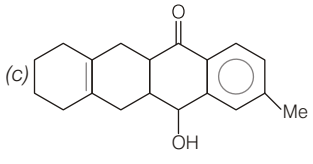


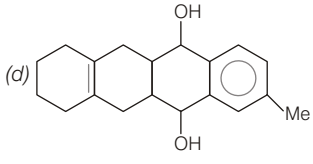
1. 

Identify compound *H*.

(a) 

(b) 

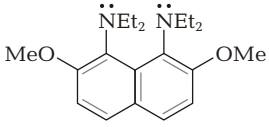
(c) 

(d) 

2. Which of the following statements are correct? Choose the correct option.

I. $CH_2Cl_2 \xrightarrow{NaOH} CH_2Cl(OH) \longrightarrow H_2C{=}O + HCl$

Reaction is a case of reduction-oxidation.

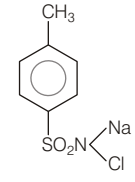
II.  is an extremely strong base towards H^+.

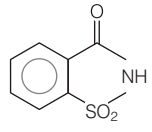
III. Azulene has an unexpectedly high dipole moment.

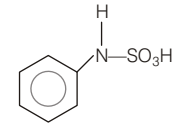
IV. CF_3^+ has planar structure.

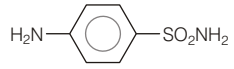
(a) I and II *(b)* III and IV *(c)* I and IV *(d)* II and III

3. Methyl cyclohexane on catalytic dehydrogenation and further treatment with chlorosulphonic acid at 370K yields a mixture of two isomers *A* and *B*. $C_7H_7SO_2Cl$. The major isomer *A* reacts with ammonia to form *C*, which on oxidation with permanganate gives compound *D*. On heating, compound *D* gives a well-known sweetening agent *E*. Identify compound *E*.

(a) 

(b) 

(c) 

(d) 

4. The radial wave equation for hydrogen atom is

$$\psi = \frac{1}{16\sqrt{4}}\left(\frac{1}{a_0}\right)^{3/2}[(x-1)(x^2-8x+12)]e^{-x/2}$$

where, $x = 2r/a_0$; a_0 = radius of first Bohr orbit.

The minimum and maximum position of radial nodes from nucleus are

(a) a_0, $3a_0$ *(b)* $\frac{a_0}{2}$, $3a_0$ *(c)* $\frac{a_0}{2}$, a_0 *(d)* $\frac{a_0}{2}$, $4a_0$

5. Which of the following statements are correct? Choose the correct option.

I. Cohesive force in metals decreases on descending a group and increases across the periodic table.

II. Electrical conductivity of a metal increases as temperature is raised but decreases for a semiconductor.

III. First ionisation energy of the transition elements are reasonably constant.

IV. Li is as strong reducing agent as caesium.

(a) Only I *(b)* I and II *(c)* I, III and IV *(d)* II, III and IV

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6. Which of the following statements are incorrect? Choose the correct option.

I. NF_3 is explosive while NCl_3 and NI_3 are stable.
II. PF_3 forms many complexes with metals while NF_3 does not.
III. Bond angles of H_2O and H_2S are nearly equal.
IV. SF_6 is unreactive towards water but TeF_6 not.

(a) I and II *(b)* III and IV
(c) I and III *(d)* II and IV

7. A steel sample is to be analysed for Cr and Mn simultaneously. By suitable treatment the Cr is oxidised to $Cr_2O_7^{2-}$ and Mn to MnO_4^-. A 10g of sample of steel is used to produce 250 mL of solution containing $Cr_2O_7^{2-}$ and MnO_4^-. A 10 mL portion of this solution is added to a $BaCl_2$ solution and by proper adjusting the acidity, the Cr is precipitated as $BaCrO_4$, 0.0549 g is obtained. A second 10 mL of the solution requires exactly 15.95 mL of 0.0750 M standard Fe^{2+} solution for its titration in acidic solution. Calculate the % Mn and % Cr in the steel sample. (Ba = 137, Cr = 52 and Mn = 55)

(a) 1.50 % *(b)* 1.09 % *(c)* 0.65 % *(d)* 2.82 %

8. Interstitial vacancies were created when a current of trivalent gaseous boron was passed through a germanium crystal decreasing density of the crystal due to part replacement of germanium by boron. In such experiment, boron atoms were found to be 150 ppm by weight in 1g of Ge crystal decreasing density by 4%. Calculate the % of missing vacancies in germanium crystal, which are filled by boron atoms. (Atomic mass of Ge = 72.6 and B = 11)

(a) 1.44 % *(b)* 2.37 % *(c)* 3.15 % *(d)* 4.74 %

9. The specific conductivity of 0.001 M Na_2SO_4 solution is 2.6×10^{-4} S cm^{-1} and it increases to 7.0×10^{-4} S cm^{-1}, when the solution is saturated with $CaSO_4$. The molar conductivities of Na^+ and Ca^{2+} ions are 50 and 120 S cm^2/mol respectively. Calculate solubility product of $CaSO_4$ solution. Specific conductivity of water used is 5×10^{-7} S cm^{-1}.

(a) 2.46×10^{-6} *(b)* 4.03×10^{-6}
(c) 4.41×10^{-6} *(d)* 2.57×10^{-6}

10. A buffer solution is prepared by placing 500 mL of water in a 1.0 L graduated cylinder. Next, 35 mL of concentrated phosphoric acid (14.7M) and 48 g of KOH are added to water. Filling the cylinder to the mark with water completed preparation of buffer. What is the pH of this solution? While preparing a second batch of the buffer, a technician mistakenly adds 48 g of NaOH instead of KOH. What is the pH of this buffer solution? $K_1 = 7.5 \times 10^{-3}$, $K_2 = 6.2 \times 10^{-8}$, $K_3 = 4.8 \times 10^{-13}$.

(a) 9 *(b)* 10 *(c)* 11 *(d)* 12

KNOWLEDGE Coefficient

Quizzer (No. 14)

Q. No.	a.	b.	c.	d.	Q. No.	a.	b.	c.	d.
1.	○	○	○	○	6.	○	○	○	○
2.	○	○	○	○	7.	○	○	○	○
3.	○	○	○	○	8.	○	○	○	○
4.	○	○	○	○	9.	○	○	○	○
5.	○	○	○	○	10.	○	○	○	○

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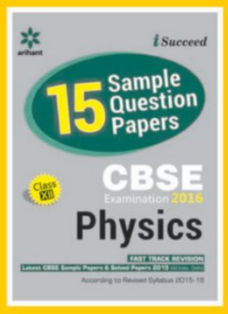

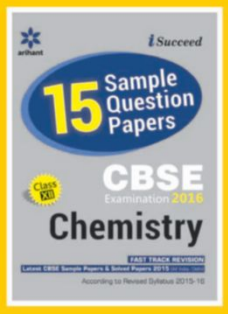

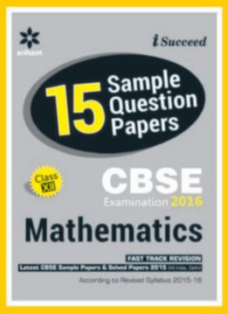

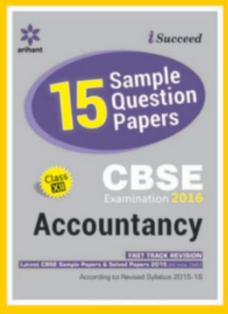

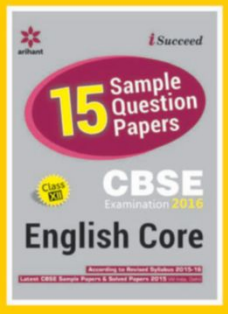

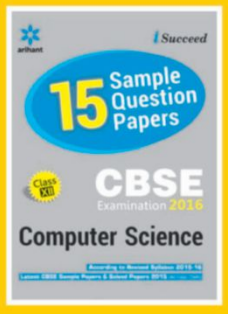

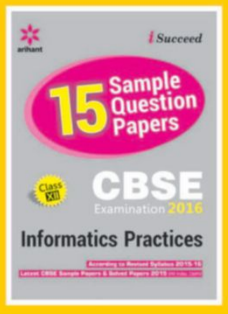

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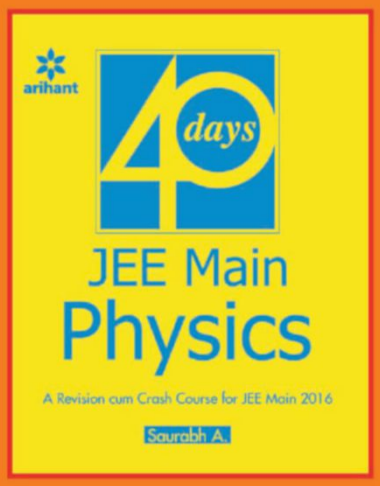

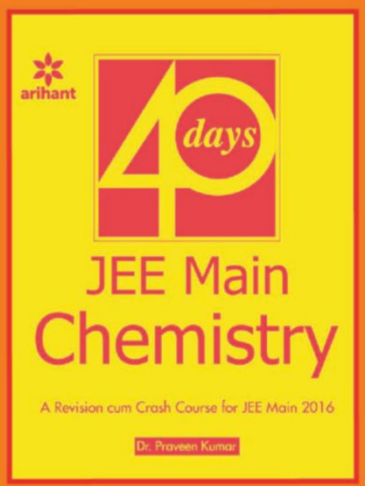

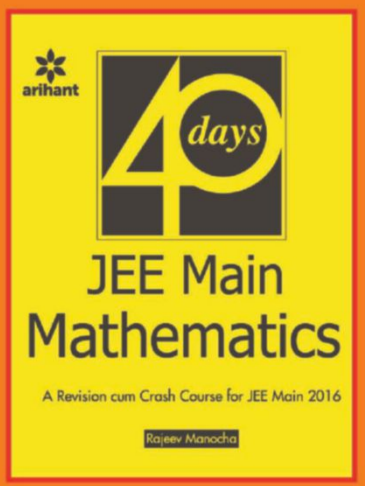

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